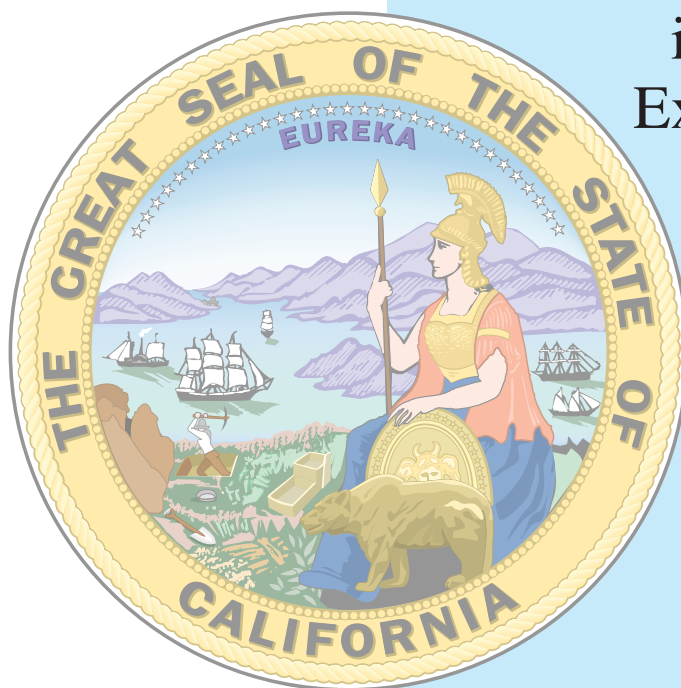


Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate

Report to the
California Environmental
Policy Council
in Response to
Executive Order
D-5-99



VOLUME 3



AIR RESOURCES BOARD

**Air Quality Impacts
of the Use of
Ethanol in California
Reformulated
Gasoline**

December 1999

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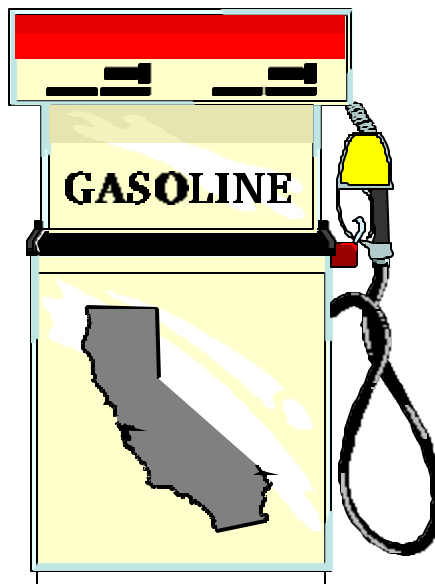
California Environmental Protection Agency



Air Resources Board

Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline

*Final Report to the California
Environmental Policy Council*



December 1999

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**State of California
California Environmental Protection Agency
AIR RESOURCES BOARD**

**Air Quality Impacts of the Use of Ethanol
in California Reformulated Gasoline**

***Final Report to the California
Environmental Policy Council***

December 1999

This report has been reviewed by the staff of the Air Resources Board, peer reviewed by the University of California, and approved by the Air Resources Board on December 9, 1999 for submittal to the California Environmental Policy Council. Mention of trade names or commercial products does not constitute endorsement or recommendation for their use. To obtain this document in an alternative format, please contact the Air Resources Board ADA Coordinator at (916) 322-4505, TDD (916) 324-9531, or (800) 700-8326 for TDD calls from outside the Sacramento area. This report is available for viewing or downloading from the Air Resources Board Internet site, <http://www.arb.ca.gov/cbg/ethanol/ethfate/ethfate.htm>.

Acknowledgments

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Principal Authors:

Bart E. Croes, P.E.
Paul Allen, P.E.
Richard Bradley, P.E.
Dongmin Luo, Ph.D.
Richard Vincent, P.E.
Luis Woodhouse, Ph.D.

Contributing Authors:

John DaMassa
Joseph De Vita
Robert Effa, P.E.
Jerry Ho, D.Env.
Eileen McCauley, Ph.D.
Hien Tran
Katarzyna Turkiewicz
Eugene Yang, Ph.D.
T.S. Yeung, Ph.D.

Special Consultants:

Dr. Daniel Grosjean, DGA, Inc.
Professor Robert A. Harley, University of California at Berkeley

Reviewed by:

Michael Scheible, Deputy Executive Officer
Robert Fletcher, Chief, Planning and Technical Support Division
Peter Venturini, Chief, Stationary Source Division
Don McNerny, Chief, Modeling and Meteorology Branch
Dean Simeroth, Chief, Criteria Pollutants Branch
Annette Hebert, Chief, Southern Laboratory Branch
Michael Carter, Chief, Emission Research and Regulatory Development Branch
Steve Brisby, Manager, Fuels Section
Mark Fuentes, Manager, Organic Analysis Section
Kathleen Nolan, Manager, Emission Research Section

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Executive Summary

Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999 calling for the removal of methyl *tertiary*-butyl ether (MTBE) from gasoline at the earliest possible date, but not later than December 31, 2002. Task 10 of the Executive Order states “the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999 for its consideration.” To assist OEHHA in its health risk assessment, we conducted an analysis to estimate the changes in outdoor air quality levels of potentially detrimental exhaust and evaporative components and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. We also included non-oxygenated gasoline in our analysis to provide a basis of comparison for the ethanol-containing gasolines. The California Energy Commission anticipates that the amount of alkylates will be increased in non-oxygenated gasoline and some ethanol-containing gasolines to replace the octane normally provided by MTBE; consequently these compounds were also a focus of our analysis.

We conducted four types of analyses: 1) a review of several recently published comprehensive assessments of the impact of oxygenated gasoline on the environment; 2) a literature review of studies that measure the direct impact of the use of ethanol in gasoline; 3) an evaluation of emission and air quality impacts from MTBE-free fuels in comparison to MTBE-containing fuel; and 4) closure of existing data gaps as part of this study and ongoing efforts that will not be complete until after the December 31, 1999 deadline in the Executive Order. These analyses led to the following conclusions.

1. In comparison to the non-MTBE components of gasoline, the atmospheric formation of toxic compounds from ethanol and alkylates are relatively slow.

Because the maximum estimated outdoor air quality levels of ethanol and alkylates are at least a factor of 10 below any level of concern identified by OEHHA, the main issues are their products of incomplete combustion and atmospheric transformations. The major products of concern for ethanol are acetaldehyde (a toxic air contaminant) and peroxyacetyl nitrate (PAN, an eye irritant and cause of plant damage). These compounds are offset by reductions in formaldehyde (a toxic air contaminant) due to the elimination of MTBE. Alkylates eventually form acetaldehyde, formaldehyde, and PAN, as do many other existing components of gasoline. The greater the atmospheric lifetime of a compound, the more dilution and dispersion will reduce the impact of products of atmospheric transformations. The atmospheric lifetime for ethanol is similar to MTBE, about two to three days under polluted conditions and longer during periods of good air quality. Atmospheric lifetimes for alkylates range from one day to a week. Our findings from theoretical calculations using airshed models with state-of-the-science chemistry indicate that other components of gasoline, such as aromatic compounds and olefins, are primarily responsible for the formation of formaldehyde, acetaldehyde, and PAN due to both their greater abundance in gasoline and their shorter atmospheric lifetimes.

- 2. The inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with a Reid vapor pressure (RVP) greater than the summertime California limit of 7.0 pounds per square inch (psi) and increased evaporative emissions of volatile organic compounds (VOCs). This effect will be mitigated by RVP reductions in the California Phase 3 Reformulated Gasoline (CaRFG3) regulations.**

Even small amounts of ethanol cause an RVP increase of about 1 psi when it is added to an ethanol-free base gasoline. Current federal law requires all gasoline sold in southern California, Sacramento, and, shortly, the San Joaquin Valley to contain an oxygenate. Under an MTBE ban, ethanol would be the only possible oxygenate with the potential for large-scale introduction. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace. California has requested the federal government for a waiver from the summertime oxygenate requirement to facilitate the phase-out of MTBE in these areas. If the waiver is granted, commingling will likely increase. Current estimates of the overall effect of commingling range from 0.1 to 0.4 psi, depending on assumptions for the market share of ethanol-containing gasolines, consumer's brand/grade loyalty, and the distribution of fuel tank levels before and after refueling events. The CaRFG3 regulations require a 0.1 psi RVP decrease to help mitigate the effect of commingling, and the Air Resources Board has committed to additional research to further quantify commingling impacts.

- 3. Ethanol-containing gasolines may lead to increases in evaporative emissions because rubber, plastics, and other materials are permeable to ethanol; moreover, ethanol may reduce the working capacity of the charcoal canisters used to control evaporative emissions on board motor vehicles. This issue has been addressed in the United States Environmental Protection Agency's (U.S. EPA's) recently adopted Tier 2 emission standards. However, the current on-road motor vehicle fleet (other than flexible-fueled vehicles operated on alcohol blends) is not fully controlled from the perspective of evaporative ethanol emissions. Further research is needed to compare the effects of ethanol, MTBE (which also reduces the working capacity of charcoal canisters), and alkylates on evaporative emission from the existing California vehicle fleet.**

Motor vehicles are subject to evaporative fuel losses from many locations in the vehicle. These losses can be described by the following three processes: running loss, hot soak, and diurnal emissions. "Running loss" emissions are evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and losses from the carbon canister (a container filled with sorbent activated carbon used to store gasoline vapors). "Hot soak" emissions are vapor losses from a recently operated hot vehicle. Most of these losses are due to permeation through hoses. "Diurnal" emissions are evaporative losses mainly from the charcoal canister and result from daily heating of the vehicle's fuel tank and consequent saturation and overflow from the canister.

Because of the tendency of ethanol to evaporate more readily than other fuel components and because the smaller size of an ethanol molecule promotes permeation through hoses, hot soak emissions tend to result in evaporative losses containing a proportionally greater amount of ethanol than was in the original fuel. Also, it is possible that ethanol's propensity to be tightly held by activated carbon, in conjunction with its hygroscopic nature (that is, it attracts water), may decrease the working capacity of the charcoal canisters used to control evaporative

emissions on board motor vehicles and result in increased diurnal emissions. However, data suggesting a reduced working capacity are somewhat conflicting in nature, but this may be partially due to the difficulty in sampling ethanol, and additional research is needed in this area.

Both early and late model-year vehicles (other than flexible-fueled vehicles operated on alcohol blends) are not fully controlled from the perspective of evaporative ethanol emissions. That is, the certification test procedures for evaporative emissions require the use of a fuel containing MTBE and, thus, do not completely take into account the use of commercially available ethanol-containing gasolines. Although more stringent evaporative emission standards were adopted in 1998 and are applicable to the 2004 to 2006 model years, the procedures were pertinent only to the fuels in use at the time of adoption and, thus, did not include ethanol blends. Revised certification test procedures to include ethanol-containing gasolines will need to be developed in order to control any incremental evaporative emissions resulting from these fuel blends. The U.S. EPA recently adopted such changes under its Tier 2 regulations.

4. Because relatively little ethanol is produced in California, it will probably all be shipped by rail or truck. The estimated statewide impact on heavy-duty truck emissions is a 0.06% increase. Most likely, these impacts will be localized at the two central ethanol distribution locations and the 64 fuel storage terminals and will be addressed locally under the California Environmental Quality Act.

The bulk of the ethanol used in California will be transported by rail from the Midwest to two central distribution locations, trucked to 64 fuel storage terminals, and then splash-blended with gasoline. The increase in heavy-duty truck emissions would be about 0.06% of the statewide total, using estimates of truck travel for ethanol distribution made by the California Energy Commission. If increased local traffic and emissions from diesel trucks become local environmental concerns, they will be addressed locally in the context of use permits and permits to operate specific facilities under the California Environmental Quality Act.

5. So long as the CaRFG3 regulations address the potential for ethanol to increase evaporative emissions and cause more rail and truck traffic, the substitution of ethanol and alkylates for MTBE in California's fuel supply will not have any significant air quality impacts. This finding is supported by theoretical calculations in the South Coast Air Basin using state-of-the-science tools, an analysis of the impact of uncertainties, air quality measurements in areas that have already introduced ethanol into their fuel supply, and an independent scientific peer review by the University of California.

We used the best available information on the emission characteristics of fuels that will be available in 2003, a comprehensive analysis of current (that is, 1997) air quality levels, and an airshed model for the South Coast Air Basin with state-of-the-science chemistry to estimate air quality in the future for the following four fuels:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG2), assumed to be equivalent in both 1997 and 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 2.0 wt% (5.7% ethanol by volume) in 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 3.5 wt% (10% ethanol by volume) in 2003.

- Non-oxygenated, fully complying CaRFG2 fuel in 2003.

Because the CaRFG3 regulations were not approved until December 9, 1999, we were unable to consider the new specifications in our emission and air quality predictions. However, because the regulations preserve the air quality benefits of CaRFG2 and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of CaRFG3 will not affect our overall conclusions.

All pollutants of concern decrease from the 1997 MTBE baseline to the 2003 MTBE baseline due to reductions in overall emissions. The predicted decreases are especially pronounced for the toxic air contaminants, ranging from 13% for formaldehyde and acetaldehyde to 33% for benzene and 43% for 1,3-butadiene. There are several differences between the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios. Because fuel-related activities are the only inventoried source of MTBE, levels of MTBE decrease 100%. Ethanol levels for the ethanol-blended gasolines increase by 48% (2.0 wt% oxygen fuel) and 72% (3.5 wt% oxygen fuel), but acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen. PAN levels are not predicted to increase for either the ethanol-blended or non-oxygenated gasolines. Benzene levels increase slightly (1%) for the ethanol-blended gasoline at 3.5 wt% oxygen with decreases predicted for the other two gasolines. All three MTBE-free gasolines produce modest reductions in 1,3-butadiene (2%) and formaldehyde (2 to 4%) levels and essentially no change in ozone, nitrogen dioxide, nitric acid, and PPN (peroxypropionyl nitrate) levels. As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average carbon monoxide levels (3%), and the 3.5 wt% oxygen ethanol-blend in lower carbon monoxide values (-9%). It should be noted that these are summertime levels—a time period when violations of the standard do not occur. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide levels within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

Primarily due to the lack of ambient air quality measurements for many of the air contaminants of concern, we were unable to predict air quality for other areas of California. However, our analysis for the South Coast Air Basin can be considered the worst-case situation in comparison to other air basins. It has the highest baseline air quality levels, the conditions most conducive to formation of secondary air pollutants (for example, ozone, acetaldehyde, and PAN), the most emissions, and the highest number of gasoline-related emission sources in California.

Calculations that bracket the impact of motor vehicle emission inventory uncertainty and chlorine atom chemistry in coastal environments resulted in increases for all pollutants, but the only significant impact on relative differences among the 2003 fuels was a large increase in ethanol for the ethanol-blended gasolines. The use of the modeling tool in a relative sense bypasses concerns about other uncertainties.

Our review of studies of the impact of the use of ethanol-containing gasoline on air quality in Denver, Colorado; Albuquerque, New Mexico; Brazil; and other areas indicates that acetaldehyde levels are substantial only in Brazil, where the fuels contained either pure ethanol or 22% ethanol, much greater levels than the maximum of 10% ethanol allowed in California gasolines. Due to the lack of RVP requirements for gasolines in Brazil, the high acetaldehyde levels could be due to the addition of substantial evaporative emissions rather than strictly the result of an ethanol-for-MTBE substitution. Even with increased acetaldehyde levels, the observed levels of PAN are more than a factor of 10 below historical levels observed in southern California although the Brazilian measurements were not in the areas likely to have the highest PAN levels.

A draft version of this report was reviewed by four scientists approved by the University of California Office of the President under a process defined by Health and Safety Code section 57004. While the reviewers agreed with our basic findings on ethanol and alkylates, they noted the need for a number of corrections, clarifications, and caveats that we have incorporated into this final version of the report. Their comments and our responses are included in this report.

6. The results of this study do not necessarily extend to other states. California does not have an RVP exemption for ethanol-containing gasolines; and the CaRFG3 Predictive Model constrains emissions of cancer-potency-weighted toxic air contaminants, oxides of nitrogen (NO_x), and VOCs. States without these safeguards (that is, non-Federal Reformulated Gasoline areas) may have significant air quality impacts from replacement of MTBE with ethanol or aromatic compounds.

A previous ARB comparison of a 10% ethanol-gasoline blend with 8.0 psi RVP and a fully complying, MTBE-based gasoline meeting a 7.0 psi RVP limit concluded that while carbon monoxide emissions decreased by about 10% for the high-RVP fuel, emissions increased for NO_x (14%), combined exhaust and evaporative VOCs (32%), ozone formation potential (17%), and cancer-potency-weighted toxic air contaminants (5%). The ozone formation potential calculations included the benefit of the carbon monoxide reduction. The results also show that there is a likelihood (between 92% and 100%) that emissions of NO_x, VOC, ozone formation potential, and cancer-potency-weighted toxics are greater with the high-RVP ethanol blend than with the fully complying gasoline. The high level of certainty associated with the results of the test program show that additional testing would not likely change the outcome of this evaluation and that additional tests on 1990 to 1995 model year vehicles and vehicles that employ control technologies similar to these are unnecessary. Thus, significant air quality impacts are likely in the parts of the United States (that is, non-Federal Reformulated Gasoline areas) where the U.S. EPA allows a 1 psi RVP exemption for ethanol.

The CaRFG3 Predictive Model constrains exhaust emissions of NO_x, VOCs, and cancer-potency-weighted toxic air contaminants (that is, acetaldehyde, benzene, 1,3-butadiene, and formaldehyde), and evaporative emissions of VOCs and benzene. Thus, different fuel formulations (for example, ethanol-blended and non-oxygenated) will be manufactured to have similar emissions through the adjustment of various fuel properties such as sulfur content, aromatic content, etc. As MTBE is removed from gasoline, the CaRFG3 Predictive Model will push California fuel suppliers toward an increased use of alkylates rather than aromatic compounds. Alkylates have no significant air quality impacts in comparison to the aromatic compounds that are powerful ozone and benzene precursors and likely to be used in other states if there is a corresponding ban on MTBE.

7. An air quality monitoring program is now in place to directly measure the impact of the phase-out of MTBE.

Our analysis of air quality impacts will be compared with field measurements that take place before and after the planned December 31, 2002, phase-out of MTBE. These types of studies were successfully conducted in California in 1996 during the implementation of CaRFG2. California's existing ambient air quality networks should be sufficient for all the criteria pollutants, MTBE, toxic air contaminants, and individual VOC compounds (that is, alkylates). Because PAN is not part of any routine air quality monitoring program, we began PAN measurements at two sites in the South Coast Air Basin last November. Because ethanol and acetaldehyde lead to PAN but not to PPN, the measurement program includes both PAN and

PPN, [and because their ratio may be a useful indicator of the impact of ethanol emissions on PAN air quality levels]. We will investigate the possibility of adding ethanol measurements and expanding the monitoring program to other areas of the State.

1. Introduction

Governor Gray Davis issued Executive Order D-5-99 on March 25, 1999 calling for the removal of methyl *tertiary*-butyl ether (MTBE) from gasoline at the earliest possible date, but not later than December 31, 2002. Task 10 of the Executive Order states “the California Air Resources Board (ARB) and the State Water Resources Control Board (SWRCB) shall conduct an environmental fate and transport analysis of ethanol in air, surface water, and groundwater. The Office of Environmental Health Hazard Assessment (OEHHA) shall prepare an analysis of the health risks of ethanol in gasoline, the products of incomplete combustion of ethanol in gasoline, and any resulting secondary transformation products. These reports are to be peer reviewed and presented to the Environmental Policy Council by December 31, 1999 for its consideration.”

1.1. Objective

The objective of this document is to meet the directives of Executive Order D-5-99. To assist OEHHA in its health risk assessment, we conducted an analysis to estimate the changes in ambient air concentrations of potentially detrimental exhaust and evaporative components and subsequent reaction products that would result from substituting ethanol-blended gasoline for gasoline blended with MTBE. We also included non-oxygenated gasoline in our analysis to provide a basis of comparison for the ethanol-containing gasolines. The California Energy Commission (CEC, 1999) anticipates that alkylates¹ will be used in non-oxygenated gasoline and some ethanol-containing gasolines in California to replace the octane² normally provided by MTBE; consequently these compounds were also a focus of our analysis.

OEHHA requested information on the following air contaminants:

- Toxic air contaminants (acetaldehyde, benzene, 1,3-butadiene, and formaldehyde).
- Criteria air pollutants [carbon monoxide (CO), nitrogen dioxide (NO₂), ozone, and particulate matter (PM₁₀, PM_{2.5})].
- Fuel oxygenates (ethanol and MTBE).
- Alkylates (C₆ to C₉ branched alkanes and cycloalkanes).
- Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN).
- Nitric acid (HNO₃).

¹ Alkylates are gasoline blendstock produced by reacting isobutane with olefins. They consist of branched alkanes, have very low aromatic content, and contain no sulfur or olefins (NESCAUM, 1999).

² MTBE has 110 octane, ethanol has 115 octane, alkylates provide 91 to 99 octane, and aromatics have 100 octane (CEC, 1999).

- Additional compounds of interest to OEHHHA (*n*-heptane, *n*-hexane, isobutene, toluene, and xylene isomers).

1.2. Scope

Our analysis addressed ambient concentrations of air pollutants that the general public would be exposed to during outdoor activities. We estimated both maximum one-hour-average and annual-average exposures. We were not able to consider indoor and personal exposures since these are a complex function of indoor-outdoor air exchange rates, proximity to gasoline-related emission sources, and personal activity.

We also did not provide estimates of pollutant deposition onto land and water surfaces. While our analysis considers dry deposition, it is only for the purpose of treating the effect of this loss process on air quality concentrations. There was no need to consider rain and other precipitation events, as air quality is generally very good under these conditions. Wet and dry deposition is being considered by the SWRCB in their ethanol fate and transport analysis for surface water and groundwater. We did not consider global warming impacts, as this is being addressed under the California Phase 3 Reformulated Gasoline (CaRFG3) regulations (ARB, 1999a; 1999d) and by the SWRCB.

1.3. Study Approach

We conducted four types of analyses. First, we reviewed several recently published comprehensive assessments of the impact of oxygenated gasoline on the environment. While the majority of these studies focused on the impact of MTBE-based gasoline, several contained information on alternative ethanol-containing and non-oxygenated gasolines. We found the prior assessments to be useful for identifying issues of concern related to air quality, but all lack a thorough review of ambient air studies in areas that introduced ethanol as a gasoline oxygenate. Thus, the second type of analysis we conducted was a literature review of studies that measure the direct impact of the use of ethanol in gasoline. Due to the already broad scope of the prior assessments, they did not conduct a comprehensive modeling and data analysis to estimate future air quality concentrations for MTBE-free fuel scenarios, although several suggested that such studies should be undertaken. In order to address this need, the third component of our study was to evaluate emission and air quality impacts for the following four fuels:

- Current MTBE-based California Phase 2 Reformulated Gasoline (CaRFG2), assumed to be equivalent in both 1997 and 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 2.0 wt% (5.7% ethanol by volume)³ in 2003.
- Ethanol-based, fully complying CaRFG2 fuel with an oxygen content of 3.5 wt% (10% ethanol by volume) in 2003.

³ The amount of an *oxygenate* such as ethanol or MTBE in gasoline is expressed as percent by volume. The amount of *oxygen* in gasoline is expressed as percent by weight (wt%). In this report, the amount of oxygenate in gasoline is referred to simply in terms of “%”, while the amount of oxygen in gasoline is referred to as “wt%”.

- Non-oxygenated, fully complying CaRFG2 fuel in 2003.

This analysis was conducted with the best available information on the emission characteristics of fuels that will be available in 2003, a comprehensive analysis of current air quality concentrations, and an airshed model with state-of-the-science photochemistry to estimate air quality in the future. Our predictions of future emissions and air quality provide only an initial estimate because of significant data gaps: 1) several uncertainties in how oil refiners will reformulate gasoline in response to California's Phase 3 regulations (ARB, 1999a; 1999d), a possible oxygenate waiver from the federal government, and market forces; 2) uncertainties in the inputs and mathematical formulation of the photochemical model; and 3) incomplete ambient measurements for some of the air contaminants. The fourth component of our analysis is to close these data gaps as part of this study and ongoing efforts that will not be complete until after the December 31, 1999 deadline in the Executive Order. We report here the results of a limited emission testing program with two commercial MTBE-free CaRFG2 gasolines that provide a reality check on the emission estimates, and progress in our long-term efforts to improve the photochemical model and collect ambient air quality data.

The following sections summarize our review of prior studies, describe emission issues related primarily to ethanol present our predictions of future emissions and air quality, and discuss uncertainties and on-going studies to address them. Three appendices contain detailed technical information on our estimates of organic gas emission profiles and emission inventories, photochemical modeling of air quality impacts, and data analysis of baseline (1997) and future (2003) air quality concentrations. A fourth appendix contains our responses to an independent scientific peer review by the University of California, comments on materials presented at public workshops on July 12, October 4, and November 10, 1999, and written and oral testimony at the public hearing of the Air Resources Board on December 9, 1999.

2. Review of Prior Studies

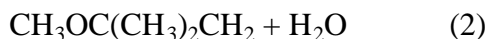
To provide a scientific foundation for our analysis, we reviewed the available literature on the atmospheric chemistry of MTBE, ethanol, and alkylates. We also reviewed eight major assessments of the impact of oxygenated gasoline on the environment conducted prior to our analysis. Ethanol has been used as the primary gasoline oxygenate in several states in the United States. In Brazil, either neat (100%) ethanol or gasohol (a mixture of ethanol and gasoline) has been used as a fuel since 1979. We conducted a literature review of ambient air studies in these areas, which provide a direct measurement of the impact of the use of ethanol in gasoline.

2.1. Atmospheric Chemistry of MTBE, Ethanol, and Alkylates

The atmospheric chemistry of MTBE, ethanol, and alkylates have already undergone extensive reviews by others. These are briefly summarized below.

2.1.1. MTBE

Atkinson (1994) has reviewed kinetic and mechanistic studies of the atmospheric chemistry of MTBE. The only significant atmospheric reaction for MTBE is with hydroxyl (OH) radicals. Two possible initial reactions are:



The rate constant for this reaction has been measured several times and the recommended value is $5.89 \times 10^{-13} (\text{T}/300)^2 e^{483/\text{T}} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240-440 K, with a rate constant of $2.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Based on several studies, the recommended reaction mechanism in the presence of NO has a product profile of *tertiary*-butyl formate (76%), formaldehyde (48%), methyl acetate (18%), and acetone (6%). *Tertiary*-butyl formate is less reactive in the atmosphere than is MTBE by about a factor of 4. Formation of *tertiary*-butyl nitrite was observed in one of the laboratory studies due to the $(\text{CH}_3)_3\text{CO} + \text{NO}$ $(\text{CH}_3)_3\text{CONO}$ reaction competing with the $(\text{CH}_3)_3\text{CO} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{CH}_3$ decomposition reaction; but under atmospheric conditions the decomposition reaction will totally dominate. The product profile is for NO being present and therefore applicable to urban areas, but possibly not to downwind areas with low NO_x concentrations. See Professor Atkinson's Comment #20 in Section D-1.1 in Appendix D for further details.

2.1.2. Ethanol

The most recent evaluations of the International Union of Pure and Applied Science (IUPAC, Atkinson *et al.*, 1997; 1999) and that of Atkinson (1994) recommend that the OH + ethanol reaction proceeds by:

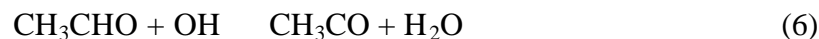


with reactions (3) and (5) each accounting for $5^{+10}_{-5}\%$ of the overall reaction at 298 K. The preferred IUPAC rate constant value for the reaction with the OH radical above is $5.56 \times 10^{-13} (\text{T}/300)^2 e^{532/\text{T}} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270-340 K, with a rate constant of $3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson *et al.*, 1999). The relative importance of reaction (5) in the IUPAC evaluations and in Atkinson (1994) is based on the assumption that H-atom abstraction from the OH group in ethanol occurs with a rate constant equal to that for the corresponding reaction in methanol. The rate constant for reaction (3) is based on an estimation and on the elevated temperature data of Hess and Tully (see the above references). In the atmosphere, reaction (4) and reaction (5) give rise to the same products (acetaldehyde plus HO_2) and are hence indistinguishable.

Reaction (5) has not been shown experimentally to be negligible under atmospheric conditions, and the only experimental data concerning the importance of the three possible reaction channels are a branching ratio of $k_4/(k_3 + k_4 + k_5) = 0.75 \pm 0.15$ at room temperature (Meier *et al.*, 1985) and an acetaldehyde yield under atmospheric conditions of $80 \pm 15\%$ (Carter *et al.*, 1979). The formation of CH_3CHOH and $\text{CH}_3\text{CH}_2\text{O}$ radicals from reactions (4) and (5) lead to the formation of acetaldehyde plus HO_2 , independent of the presence or absence of NO, and hence the data of Carter *et al.* (1979) indicate that $(k_4 + k_5)/(k_3 + k_4 + k_5) = 0.80 \pm 0.15$. Formation of HOCH_2CH_2 radicals via reaction (3) leads to the formation of glycolaldehyde (HOCH_2CHO) (22%) and HCHO (78%) in the presence of NO (yields are for 298 K and atmospheric pressure of air), and to $\text{HOCH}_2\text{CH}_2\text{OOH}$, $\text{HOCH}_2\text{CH}_2\text{OH}$, HOCH_2CHO , and HCHO in the absence of NO. Atkinson (1997) has reviewed the atmospheric reactions of the

HOCH₂CH₂ radical. Formation of methyl nitrate is not expected to be of any significance; rather the formation of ethyl nitrate in very small overall yield (<0.1%) could occur from the reaction of the ethyl peroxy radical with NO.

Once formed from the atmospheric reaction of ethanol with OH radicals, acetaldehyde is rapidly consumed by photolysis and by reaction with OH radicals. Photolysis leads to formation of CO and formaldehyde while reaction with the OH radical leads to PAN via the following process:



The acetyl (CH₃CO₃) radical also reacts with NO to form CH₃CO₂ and NO₂. In addition, PAN decomposes back to CH₃CO₃ and NO₂ in a reaction that increases at higher temperatures. Ambient concentrations of PAN are a function of ambient temperature, the NO₂-to-NO ratio, and the concentration of the acetyl radical precursor (Grosjean, 1997).

2.1.3. Alkylates

Alkylates consist of branched alkanes and cycloalkanes, mostly with six to nine carbons such as iso-octane (2,2,4-trimethylpentane) and methylcyclopentane. The atmospheric chemistry of alkanes was most recently reviewed by Atkinson (1997). Under atmospheric conditions, the potential reaction pathways for alkylates include gas-phase reactions with OH and nitrate (NO₃) radicals. The gas-phase reactions of alkylates with ozone are of negligible importance.

Kinetic studies have been carried out for several alkylates and the rate constants with OH radicals obtained range from (1 to 10)×10⁻¹² cm³molecule⁻¹s⁻¹ at 298 K (Atkinson, 1997). The measured rate constants of selected alkylates with NO₃ radicals range from (0.5 to 4.0)×10⁻¹⁶ cm³molecule⁻¹s⁻¹ at 298 K. The products observed and expected in the presence of NO include carbonyls, alkyl nitrates, hydroxycarbonyls, and hydroxynitrates. At low NO_x concentrations, the expected products include hydroperoxides, alcohols, hydroxycarbonyls, diols, and hydroxyhydroperoxides (Atkinson, 1997).

2.1.4. Atmospheric Lifetime and Ozone Formation Potential

Table 2.1 lists the calculated atmospheric lifetimes of MTBE, ethanol, and alkylates due to gas-phase reaction with OH radicals. The calculation was based on the IUPAC-recommended OH rate constants and an ambient OH radical concentration of 3.0×10⁶ molecule/cm³, representative of moderately polluted conditions in Los Angeles (George *et al.*, 1999). Maximum incremental reactivities (MIRs) -- measures of ozone formation potential -- of MTBE, ethanol, and alkylates were obtained from a recent reactivity assessment (Carter, 1999a). For comparison purposes, the composite MIR for gasoline exhaust is 3 to 4 g ozone/g VOC.

Table 2.1. Calculated Atmospheric Lifetimes Due to Gas-Phase Reaction with OH Radicals and MIRs for MTBE, Ethanol, and Alkylates

| Compound | Atmospheric Lifetime ^a (daylight hours) | Maximum Incremental Reactivity ^b (g ozone/g VOC) |
|-----------|---|--|
| MTBE | 32 | 0.88 |
| Ethanol | 28 | 1.88 |
| Alkylates | 9-93 | 1.0-2.3 |

^aFor a 12-hour daytime-average OH radical concentration of 3.0×10^6 molecule/cm³.

^bFrom Carter (1999a), using the techniques described in Carter (1994).

2.1.5. Chlorine Chemistry

There is an increasing recognition (e.g., De Haan *et al.*, 1999) that chlorine (Cl) atoms may play a role in the oxidation of organics in coastal areas. Several measurements of Cl₂ and photolyzable chlorine compounds in coastal areas in the eastern U.S. find nighttime concentrations of Cl₂ (and perhaps other species) of ~150 ppt (e.g., Spicer *et al.*, 1998). At dawn, photolysis generates highly reactive chlorine atoms at concentrations of up to ~10⁵ molecule/cm³. The Cl + MTBE rate constant is 1.66×10^{-10} cm³molecule⁻¹s⁻¹ (Wallington *et al.*, 1988) and the Cl + ethanol rate constant preferred by the IUPAC is 9.0×10^{-11} cm³molecule⁻¹s⁻¹ (Atkinson *et al.*, 1999), corresponding to lifetimes of 30 and 17 hours, respectively, at a Cl atom concentration of 10⁵ molecule/cm³. The rate constants for the reaction of selected alkylates with Cl atoms range from $(1.75 \text{ to } 3.9) \times 10^{-10}$ cm³molecule⁻¹s⁻¹ (Atkinson, 1997), corresponding to lifetimes of 16 to 7 hours at a Cl atom concentration of 10⁵ molecule/cm³. Thus, Cl atom reactions will compete with OH radical-initiated reactions for these compounds in coastal areas during daylight hours. Product studies suggest that hydrogen abstraction in MTBE, ethanol, and alkylates is the major reaction pathway for Cl atoms as for OH radicals (Carter *et al.*, 1979).

2.1.6. Conclusions from Review of Atmospheric Chemistry

The major atmospheric loss process for MTBE, ethanol, and alkylates is reaction with OH radicals, which is relatively slow. Photolysis and reactions of these compounds with ozone and NO₃ radicals in the atmosphere are slow and of negligible importance. Reactions with Cl atoms in coastal areas may be important. Product studies showed that the major products in the presence of NO_x are *tertiary*-butyl formate, formaldehyde, and methyl acetate from MTBE, acetaldehyde and PAN from ethanol, and carbonyls, alkyl nitrates, hydroxycarbonyls, and hydroxynitrates from alkylates.

2.2. Recent Assessments of the Impact of Oxygenated Gasoline on the Environment

We reviewed eight major assessments of the impact of oxygenated gasoline on the environment that were conducted prior to our analysis. We focused our review on air quality issues and do not report conclusions on health, water quality, fuel supply, political, and other

topics that were not the subject of our analysis. The reports are summarized below in order of their applicability to the scope of our analysis.

2.2.1. University of California MTBE Report

Governor Wilson signed Senate Bill S.B. 521 into law on October 8, 1997, enacting the MTBE Public Health and Environmental Protection Act of 1997. This legislation appropriated \$500,000 to the University of California for a comprehensive assessment of the current health and environmental impacts of MTBE use in California (Keller *et al.*, 1998). Their findings formed the basis for Executive Order D-5-99 issued by Governor Gray Davis that precipitated our ethanol fate and transport analysis. The University of California associated decreased automotive CO emissions and increased emissions of formaldehyde, isobutene, and unburned MTBE with MTBE-based CaRFG2 (Koshland *et al.*, 1998). They concluded that the MTBE atmospheric reaction product *tertiary*-butyl formate (see Section 2.1.1) is not formed as a combustion byproduct.

The University of California review of emission studies for ethanol-containing gasoline (Koshland *et al.*, 1998) concluded that 10% ethanol results in statistically significant changes in exhaust emissions of CO (13% reduction), VOC (6% reduction), NO_x (5% increase), acetaldehyde (159% increase), and benzene (11% reduction), as well as increases in evaporative emissions. However, these findings are not applicable to fully complying CaRFG2 fuels that are subject to the same Reid vapor pressure (RVP)⁴ requirement and are constrained by the ARB Predictive Model (ARB, 1995) to meet the same limits on exhaust emissions of VOC, NO_x, and cancer risk-weighted toxic air contaminants. For these fully complying gasolines, Koshland *et al.* (1998) concluded that MTBE and other oxygenates have no significant effect on exhaust emissions from advanced technology vehicles, nor is there a statistically significant difference in the emission reduction of benzene from oxygenated and non-oxygenated CaRFG2 fuels. Keller *et al.* (1998) expressed concerns about increased ethanol emissions, and recommended modeling studies to predict the air quality concentration increases of acetaldehyde and PAN that would be expected to result from the large-scale substitution of ethanol for MTBE. This recommendation is implemented in Section 4.2.

2.2.2. Air Resources Board

As provided for in Health and Safety Code Section 43830(g), the ARB (1998b) investigated whether a 10% ethanol gasoline blend with 8.0 psi RVP would provide as good or better emission benefits as a fully complying, MTBE-based gasoline blended to be typical of the gasoline used during the summer and meeting a 7.0 psi RVP limit. An exhaust emission test program was conducted with 12 light-duty vehicles, and six of the vehicles were also tested for hot-soak and diurnal evaporative emissions. Running loss emissions were estimated with the assistance of General Motors using their vapor generation model, and with draft evaporative emissions models from the ARB and the USEPA.

⁴ Reid vapor pressure is a measure of the gas pressure a liquid/gas system will exert to a closed system when heated to 100 F, measured in pounds per square inch (psi). Gasolines with a higher RVP are more volatile than those with a lower RVP, and thus have a greater propensity to evaporate.

A formal statistical analysis indicated that CO emissions decreased by about 10% for the high-RVP ethanol blend with increases in NO_x (14%), combined exhaust and evaporative NMOG (32%), ozone formation potential (17%), and potency-weighted toxic air contaminants (5%). The ozone formation potential calculations included the benefit of the CO reduction. The toxic compounds evaluated under this test program were benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. The results also show that there is a likelihood between 92% and 100% that emissions of NO_x, NMOG, ozone formation potential, and potency-weighted toxics are greater with the high-RVP ethanol blend than with the fully complying gasoline. The data also show that the likelihood is almost 100% that CO emissions are higher with the fully complying gasoline than with the high-RVP ethanol blend. The high level of certainty associated with the results of the test program show that additional testing would not likely change the outcome of this evaluation and that additional tests on 1990 to 1995 model year vehicles and vehicles that employ control technologies similar to these are unnecessary. Based on these results, the ARB determined that an RVP exemption should not be granted to 10% ethanol blends.

2.2.3. U.S. EPA Blue Ribbon Panel on Oxygenates in Gasoline

U.S. EPA Administrator Carol Browner appointed a Blue Ribbon Panel in November 1998 to investigate the air quality benefits and water quality concerns associated with oxygenates in gasoline, and to provide independent advice and recommendations on ways to maintain air quality while protecting water quality (U.S. EPA, 1999). Similar to the requirement in the Executive Order, the Blue Ribbon Panel concluded that the U.S. EPA should conduct a full, multi-media assessment (on air, soil, and water) of any major new additive to gasoline prior to its introduction. They also recommended the establishment of routine and statistically valid methods for assessing the actual composition of reformulated gasoline and its air quality benefits, including the development of field monitoring and emissions characterization techniques to assess the “real world” effects of different blends on emissions. These types of studies were already conducted in California during the implementation of CaRFG2 in 1996 (Kirchstetter and Harley, 1999ab; Gertler *et al.*, 2000; Larsen, 2000), and we describe a similar program for Phase 3 reformulated gasoline in Section 5.3. The Blue Ribbon Panel also presented information on increased evaporative emissions from commingling of ethanol-containing and non-ethanol gasolines. This issue will be discussed in Section 3.4.5.

2.2.4. Northeast States for Coordinated Air Use Management

In response to a request from the New England Governor’s Conference, the Northeast States for Coordinated Air Use Management (NESCAUM) investigated the air quality, fuel supply, and cost impacts of MTBE and its alternatives (NESCAUM, 1999). They identified ethanol, aromatics, and alkylates as the likely replacements for MTBE. NESCAUM reported that combustion of ethanol-blended gasoline results in a 70% increase of acetaldehyde emissions, although the basis for this statement is not referenced. Concerns were also expressed for substantially increased toxic emissions if aromatics were used to replace MTBE. Although NESCAUM identified alkylates as an MTBE substitute that would not increase toxic emissions, they recommended that a rigorous evaluation of combustion byproducts and environmental fate and transport should be conducted before increasing its use in gasoline. They also presented information on increased evaporative emissions from commingling of ethanol-containing and non-ethanol gasolines. This issue will be discussed in Section 3.4.5.

2.2.5. National Research Council

At the urging of some members of the United States Congress, the U.S. EPA arranged for the National Research Council (NRC) to conduct a comparison of the ozone formation potential of MTBE and ethanol as gasoline oxygenates (NRC, 1999). The NRC found that the ozone formation potential (as measured with the California MIR scale) of exhaust emissions from motor vehicles operating on ethanol-blended gasoline were lower -- but not significantly lower -- than from motor vehicles using MTBE-blended gasoline. The NRC also concluded that the mass and ozone formation potential (per mile) of evaporative emissions from motor vehicles fueled with ethanol-blended gasoline were significantly higher, and that this increase would be detrimental to air quality in terms of ozone. This latter finding was attributed to an RVP increase of 1 psi from splash blending the ethanol-containing gasoline, and is consistent with the conclusions of the earlier ARB (1998b) analysis using the same vehicle test data. However, these findings are not applicable to the fully-complying ethanol-blended gasolines that need to meet the same RVP requirements as MTBE-blended gasolines that are under study in the current analysis.

2.2.6. National Research Council of Canada

The National Research Council of Canada estimated the relative impacts of an industry-average gasoline and a gasoline containing 10% ethanol (E10) and having about a 1 psi greater RVP (Singleton *et al.*, 1997). They used a photochemical box model to project air quality in 1995 with model scenarios based on the ozone episode of August 1 to 4, 1988 in southern Ontario. The ethanol-blended fuel results in an overall change of emissions for VOC (9% increase) and CO (15% decrease), with no change in NO_x. This leads to increases in concentrations of ozone (0.4 to 1.6%), formaldehyde (1.0 to 1.5%), acetaldehyde (about 2.7%), and PAN (2.9 to 4.5%), and an approximate 15% reduction in CO concentrations (Singleton *et al.*, 1997). The light-duty gasoline vehicle contribution to the 24-hour-average secondary formaldehyde and acetaldehyde concentrations was 10 to 18% and 28 to 36% greater, respectively, for the ethanol blend. The light-duty gasoline vehicle contribution to PAN was 12 to 18% greater for the E10 gasoline than that for industry-average gasoline. As with the NRC study, these results for non-complying gasolines are not germane to CaRFG2.

2.2.7. American Methanol Institute

The American Methanol Institute funded Malcolm Pirnie, Inc. (1998) to evaluate the fate and transport of ethanol in the environment. The primary focus of the report was on soil and groundwater impacts, and the air quality analysis consisted entirely of a literature review. Based primarily on the ARB (1998b) analysis of a non-complying ethanol-containing gasoline with a 1 psi RVP increase, they concluded that ethanol will lead to reduced CO emissions and increased VOC, NO_x, and acetaldehyde emissions with overall detrimental results on ozone and PAN concentrations.

2.2.8. Governors' Ethanol Coalition

A recent ethanol fate and transport study funded by the 22-state Governors' Ethanol Coalition (Ulrich, 1999) focused primarily on the impact on subsurface and surface water quality and placed only cursory attention on air quality issues. The report recommended that additional information on air quality issues should be considered, including whether PAN concentrations increased with ethanol-blended gasolines.

2.2.9. Conclusions from Review of Recent Assessments

The majority of these studies focused on the impact of MTBE-based gasoline, but several discussed issues related to ethanol-containing and non-oxygenated gasolines as an alternative to MTBE. We found the prior assessments to be useful for identifying issues of concern, but all lacked a thorough review of ambient air studies in areas that had introduced ethanol as a gasoline oxygenate. Due to the already broad scope of the prior assessments, they did not conduct a comprehensive modeling and data analysis to estimate future air quality concentrations for MTBE-free fuel scenarios, although several suggested that such studies should be undertaken. Both these needs are addressed in subsequent sections.

2.3. Ambient Air Quality Studies

We reviewed a total of sixteen journal articles and other documents that reported ambient air measurements in areas that used ethanol as a gasoline oxygenate. Studies conducted in Denver, Albuquerque, and Brazil provided the most useful insights to the future situation in California. The primary focus of these studies was on the change in ambient concentrations of acetaldehyde and PAN. Studies carried out in Alaska (Backer *et al.*, 1997) and Arizona (MathPro and EEA, 1998; Zielinska *et al.*, 1998) were not as useful because they did not include measurements before the introduction of ethanol or they did not include ambient air quality impacts. In Las Vegas and Chicago, ambient measurements of aldehydes and PAN were not conducted either before or after ethanol introduction.

2.3.1. Denver, Colorado

The Denver metropolitan area is the first region in the United States to implement the use of oxygenated gasoline in an effort to reduce ambient CO (Anderson *et al.*, 1994). The program has been mandated since the beginning of 1988 when the majority of the fuel sold contained 8% MTBE with the rest being a 10% ethanol blend. Since then, the additive used has gradually shifted from largely MTBE to largely ethanol. Anderson *et al.* (1997) reported that the concentrations of formaldehyde and acetaldehyde during the winter of 1995/96, when nearly all of the gasoline was blended with ethanol, were not significantly different from those measured during the winter of 1988/89 when 95% of the gasoline was blended with MTBE. They concluded that photochemical production and destruction of these aldehydes suppress the effect of emission changes.

2.3.2. Albuquerque, New Mexico

Albuquerque is one of the urban areas in the United States mandated to use oxygenated gasoline blends for improving air quality during the winter months. In the winter, over 99% of the gasoline contains 10% ethanol. Gaffney *et al.* (1997; 1998) examined the air quality impacts of ethanol-blended gasoline by measuring the ambient concentrations of PAN and aldehydes in the summer of 1993 (prior to the introduction of ethanol-blended gasoline) and in the winters of 1994 and 1995 (after the introduction of ethanol-blended gasoline). Compared to the summertime data, they observed a 10% acetaldehyde increase during one winter, but a significant decrease (lower by a factor of five) in the other winter. The study observed an increase of PAN by a factor of two and four, respectively, in both winters that the authors attributed to the use of ethanol-containing gasoline. However, as pointed out by Whitten (1998), the study conducted

by Gaffney *et al.* (1997; 1998) is not a convincing case for demonstrating the air quality impact of ethanol-containing gasoline. The major drawbacks are the lack of control conditions (i.e., no data for pre-ethanol wintertime conditions) and meteorological variation. For example, average concentrations of PAN varied by a factor of two between the two winters, largely due to meteorology.

2.3.3. Brazil

Brazil is the only country in the world where a national, large-scale ethanol fuel program has been implemented. The ethanol fuel was first introduced in 1979 and its use has increased steadily since then. In 1997, approximately nine million automobiles in Brazil ran on a gasohol fuel (gasoline blended with 22% ethanol) and another four million ran on neat (100%) ethanol (Grosjean, 1997). Grosjean *et al.* (1990) measured ambient concentrations of aldehydes in three major urban cities of Brazil -- San Paulo, Rio de Janeiro, Salvador -- from 1986 to 1988 and reported that acetaldehyde was the most abundant carbonyl in terms of its maximum concentration (35 ppb), followed closely by formaldehyde (34 ppb). The results also showed that acetaldehyde concentrations in urban areas of Brazil were substantially higher than those measured elsewhere in the world, most likely caused by large-scale use of ethanol as a vehicle fuel. In contrast, the ambient concentrations of formaldehyde showed a small increase compared to those measured elsewhere. More recently, deAndrade *et al.* (1998) reported that the concentrations for formaldehyde and acetaldehyde measured in Salvador, Brazil ranged from 0.20 to 80 ppb and from 0.40 to 93 ppb, respectively. Tanner *et al.* (1988) observed up to 5 ppb of PAN, which they attributed to high ambient concentrations of acetaldehyde. These observations also agreed with model calculations of the photochemical processes. In addition, Grosjean and coworkers (1998a; 1998b; 1999a) measured ambient concentrations of ethanol and MTBE in Porto Alegre, Brazil from March 1996 to April 1997. Ambient concentrations of ethanol and MTBE ranged from 0.4 to 68.2 ppb and 0.2 to 17.1 ppb, respectively. Since there were no ambient data available prior to the use of ethanol-containing gasoline, these studies could not evaluate the direct impact on air quality before and after the introduction of ethanol into the fuel.

2.3.4. Conclusions from Review of Ambient Air Quality Studies

The studies of the impact of the use of ethanol-containing gasoline on air quality conducted in Denver, Albuquerque, and Brazil are not comprehensive but provide useful insight in how to design an ambient air monitoring program to directly measure the air quality impact of an MTBE phase-out (see Section 5.3). The impact on acetaldehyde concentrations is substantial only in Brazil, where the fuels contain either neat ethanol or 22% ethanol. Due to the lack of RVP requirements for gasolines in Brazil, this acetaldehyde increase could be due to the addition of substantial evaporative emissions rather than strictly the result of an ethanol-for-MTBE substitution. Even with increased acetaldehyde concentrations, the observed PAN concentrations are modest and more than a factor of 10 below historical levels observed in southern California (Grosjean, 1999b) although the Brazilian measurements were not in the areas likely to have the highest PAN levels

3. Emission Issues

A number of issues related to emissions from vehicles operated on MTBE-free gasolines emerged from our review of prior assessments and comments from the public. Various emissions associated with fuel additives and transportation of ethanol, and the possible increased evaporative emissions due to ethanol's high volatility, will need to be addressed with the Phase 3 Reformulated Gasoline specifications and other regulatory programs if they are found to be significant. This section does not include a full discussion of exhaust emissions, as we were able to determine the effect of MTBE-free fuels on exhaust using the automotive emission estimation procedures described in Section 4.1.

3.1. California Phase 3 Reformulated Gasoline Regulations

Executive Order D-5-99 directs the ARB to adopt Phase 3 Reformulated Gasoline (CaRFG3) regulations by December 1999. The directive specified that the CaRFG3 regulations should provide additional flexibility in lowering or removing oxygen, maintain current emission and air quality benefits from the CaRFG2 regulations, and allow compliance with the State Implementation Plan for achieving ambient air quality standards. On December 9, 1999, the Air Resources Board approved amendments to CaRFG2 in response to the Executive Order. The approved amendments include a prohibition on the use of MTBE in gasoline, revised specifications for Phase 3 reformulated gasoline, and an improved and expanded Predictive Model (ARB, 1999a; 1999d). Table 3.1 summarizes the approved amendments to the flat, averaging, and cap limits of various fuel properties compared with the existing CaRFG2 limits. Because the CaRFG3 regulations were not approved until December 9, 1999, we were unable to consider the new specifications in our emission and air quality predictions. However, because the regulations preserve the air quality benefits of CaRFG2 and apply equally to ethanol-blended and non-oxygenated gasolines, consideration of CaRFG3 will not affect our overall conclusions.

Table 3.1. Approved Amendments to the CaRFG2 Property Limits

| Property | Flat Limits | | Averaging Limits | | Cap Limits | |
|----------------------|-------------|--------------------|-------------------|-----------|------------|----------------------|
| | CaRFG2 | CaRFG3 | CaRFG2 | CaRFG3 | CaRFG2 | CaRFG3 |
| RVP, psi, max | 7.0 | 7.0 ⁽¹⁾ | na ⁽²⁾ | no change | 7.0 | 6.4-7.2 |
| Benzene, vol%, max | 1.00 | 0.80 | 0.80 | 0.70 | 1.20 | 1.10 |
| Sulfur, ppmw, max | 40 | 20 | 30 | 15 | 80 | 60/30 ⁽³⁾ |
| Aromatics, vol%, max | 25 | no change | 22 | no change | 30 | 35 |
| Olefins, vol%, max | 6.0 | no change | 4.0 | no change | 10 | no change |
| Oxygen, wt% | 1.8 to 2.2 | no change | na ⁽²⁾ | no change | 0-3.5 | 0-3.7 ⁽⁴⁾ |
| T50 °F, max | 210 | 213 | 200 | 203 | 220 | 220 |
| T90 °F, max | 300 | 305 | 290 | 295 | 330 | 330 |

(1) Equal to 6.9 psi if using the evaporative element of the Predictive Model.

(2) Not applicable.

(3) 60 ppmw will apply December 31, 2002; 30 ppmw will apply December 31, 2004.

(4) If the gasoline contains more than 3.5 wt% but no more than 10% ethanol, the cap is 3.7 wt%.

3.2. Fuel Additives

3.2.1. Denaturants

Denaturants comprise from 0.2 to 0.5 wt% of ethanol. Generally, they are gasoline or gasoline-blending materials. Therefore, they should not add any chemical species that are not already present in gasoline. There would be a small potential for denaturant at 0.5 wt% in ethanol to cause the final blended gasoline to violate the CaRFG2 regulatory limits and thereby cause slight increases in emissions. However, the potential for non-complying product always exists. That potential is limited by the ARB field inspection of gasoline, whatever may be the cause of non-compliance.

3.2.2. Co-Solvents

Co-solvents refer to a bulk additive to ethanol other than the denaturant. To our knowledge, no such additives are used. If one were added, it would be constrained by ASTM D 4806-98 “Denatured Fuel Ethanol for Blending with Gasoline” to comprise less than 7.4% of the ethanol, and it could not contain pyroles, turpentine, ketones, or tars. Also, ASTM D 4806-98 excludes the addition of any aliphatic alcohol or ether to ethanol unless that species has been shown to cause no harm to fuel systems.

3.3. Emissions Associated with Transportation of Ethanol

Since relatively little ethanol is produced in California, it will probably all be transported by rail from the Midwest to two central distribution locations, trucked to 64 fuel storage terminals, and then splash-blended with gasoline. The increase in heavy-duty truck emissions would be about 0.06% of the statewide total, using estimates of truck travel for ethanol distribution made by the California Energy Commission (ARB, 1999a). If increased local traffic and emissions from diesel trucks become local environmental concerns, they will be addressed locally in the context of use permits and permits to operate specific facilities under the California Environmental Quality Act.

3.4. Automotive Evaporative Emissions

3.4.1. Evaporative Processes

Motor vehicles are subject to evaporative fuel losses from many locations in the vehicle. These losses can be described by the following three processes: running loss, hot soak, and diurnal emissions. “Running loss” emissions are evaporative emissions which occur during operation of the vehicle and stem from permeation through the fuel hoses and losses from the carbon canister (a container filled with sorbent activated carbon used to store gasoline vapors). “Hot soak” emissions are vapor losses from a recently operated hot vehicle. Most of these losses are due to permeation through hoses. In older vehicles, the carburetor bowl is a prime source of hot soak emissions. “Diurnal” emissions are evaporative losses mainly from the carbon canister and result from daily heating of the vehicle’s fuel tank and consequent saturation and overflow from the canister.

3.4.2. Ethanol Evaporative Emissions

Direct evaporation of an ethanol-containing gasoline tends to result in emissions containing a greater proportion of ethanol than the original fuel. For example, a gasoline with an RVP of 8.0 psi and containing 10 wt% ethanol will evaporate over a period of 2 hours into a vapor containing approximately 13 wt% ethanol (Grisanti *et al.*, 1995). On the other hand, a determination of vapor composition from an emitting vehicle is difficult since the evaporative source (whether a rubber hose or a canister) will affect vapor composition. All else being equal, one would expect that the tendency of ethanol to evaporate more readily than other fuel components should result in a greater proportion of ethanol in emissions measured by standard motor vehicle test procedures. Hot soak emissions from a test program conducted by ARB (1998b) using a blend of 10% ethanol with an RVP of 7.8 psi confirmed that the proportion of ethanol in the vapor was higher than in the fuel. In this case, the proportion of ethanol in the vapor was on the order of 25 to 50 wt% (ARB, 1998b). Increases of similar magnitude were seen in earlier studies (Furey and King, 1980). These exceptionally high levels are likely due to the high permeability of rubber hoses with respect to ethanol (Furey and King, 1980). However, it is not clear if there is a problem with the hosing materials used in the existing vehicle fleet. In summary, hot soak emissions tend to result in evaporative losses containing a proportionally greater amount of ethanol than was in the original fuel. The use of materials non-permeable to ethanol is an area requiring further research and development.

3.4.3. Impact of Ethanol-Containing Gasoline on Canister Function

The carbon canister is a primary component of the evaporative emission control system. Filled with sorbent activated carbon, it is designed to readily adsorb and release VOC vapors. During vapor generation (e.g., gasoline evaporation from a hot fuel tank), the canister receives and stores vapors. If saturated, the canister will vent excess vapors to the atmosphere. During vehicle operation, the canister is purged, with the vapor routed to the engine's intake manifold for combustion.

The amount of fuel vapor a canister can hold and subsequently release is designated the working capacity. Different chemical species are retained by the canister to different degrees. Oxygenates such as ethanol and MTBE bind more tightly to the activated carbon than hydrocarbons such as butane and isopentane (Furey and King, 1980). This may have the effect of reducing the canister's working capacity. Additionally, ethanol is hygroscopic (i.e., attracts water), and water is clearly known to reduce working capacity (Manos *et al.*, 1977). In summary, it is possible that ethanol's propensity to be tightly held by the activated carbon in conjunction with its hygroscopic nature may result in increased diurnal emissions. Data suggesting a reduced working capacity are somewhat conflicting in nature, but this may be partially due to the difficulty in sampling ethanol (Grisanti *et al.*, 1995). Additional research is needed in the area.

3.4.4. Impact of Ethanol-Containing Gasoline on In-Use Evaporative Emissions

The ethanol evaporative emissions associated with a particular vehicle will depend on that vehicle's technology and the stringency of its emission standards. Flexible-fueled vehicles (FFV) in California will be controlled for their evaporative emissions of ethanol since they must be certified on the appropriate test fuel. For example, a FFV certified to gasoline/ethanol will be certified to E10 (10% ethanol), which is a worst-case blend from the standpoint of evaporative

emissions. Both early and late model-year vehicles other than FFVs are not controlled from the perspective of evaporative ethanol emissions, i.e., the certification test procedures for evaporative emissions do not take into account the use of commercially available ethanol-containing gasolines. Although more stringent evaporative emission standards were adopted in 1998 and applicable to the 2004 to 2006 model years, the procedures were pertinent only to the fuels in use at the time of adoption and, thus, did not include ethanol blends. Revised certification test procedures to include ethanol-containing gasolines will need to be developed in order to control any incremental evaporative emissions resulting from these fuel blends. The U.S. EPA recently adopted such changes under its Tier 2 regulations.

3.4.5. Impact of Commingling of Ethanol-Containing and Ethanol-Free Gasolines

Even small amounts of ethanol cause an RVP increase of about 1 psi when it is added to an ethanol-free base gasoline. To account for this unique property of ethanol, all ethanol-containing CaRFG2 is blended with base gasoline that has an RVP of about 6.0 psi (by reducing high RVP components, such as pentanes and butanes) to produce a fuel that complies with the 7.0 psi limit. However, even if such a low RVP blendstock is used, the inadvertent commingling of ethanol-containing and ethanol-free gasolines in vehicle fuel tanks results in a combined gasoline with an RVP greater than 7.0 psi and increased evaporative VOC emissions. For example, in a 50-50 commingled blend where E10⁵ with an RVP of 7.0 psi is added to an equivalent volume of a ethanol-free gasoline with the same 7.0 psi RVP, the resulting RVP is about 7.5 psi and not the 7.0 psi as would be expected when two ethanol-free gasolines are commingled.⁶ Aulich and Richter (1999) confirmed that commingling does increase RVP and evaporative VOC emissions. The ethanol RVP increase was most pronounced in blends of 5 to 35% E10 and less pronounced once the gasoline blends exceeded a 50% E10 mixture. Gasoline with 2% ethanol, or a mixture of 80% gasoline with 20% E10, showed RVP increases of 0.66 to 0.93 psi over the base fuel RVP. Aulich and Richter (1999) used gasolines with relatively high RVPs (9.85 and 9.9 psi) compared with the CaRFG2 limit of 7.0 psi, so clearly additional research is needed with CaRFG2-complying fuels.

As reported by the Blue Ribbon Panel (U.S. EPA, 1999), many factors are extremely important in determining the overall effect of commingling. These include the market share of ethanol-containing gasolines, station/brand loyalty, and the distribution of fuel tank levels before and after a refueling event. Caffrey and Machiele (1994) attempted to take these variables into

⁵ A gasoline containing 10% ethanol by volume.

⁶ Commingling these two gasolines is equivalent to first combining the non-ethanol portion of both gasolines and then adding ethanol. The ethanol-free gasoline by definition has an RVP of 7.0 psi. The non-ethanol portion of the ethanol-containing gasoline had to have an RVP of 6.0 psi (since the subsequent addition of the ethanol produced a gasoline with an RVP of 7.0 psi). The non-ethanol components combine linearly producing a new fuel component having an RVP of about 6.5 psi (halfway between 6.0 and 7.0 psi). Then, adding in the ethanol component, which would now be about 5% of the final blend, increases the RVP to about 7.5 psi. It is important to note that although the new 50-50 commingled blend would have an ethanol content of around 5%, not 10% as in the original ethanol-containing gasoline, the full 1.0 psi RVP increase would still occur (U.S. EPA, 1999).

account in modeling the effect of commingling in a mixed fuel marketplace. Their conclusions include the following:

- Brand loyalty and ethanol market share are much more important variables than the distribution of fuel tank levels before and after a refueling event.
- Depending on the combination of variables chosen, the overall effect of commingling in an MTBE-free market range from under 0.1 psi to over 0.4 psi.
- The effects of the increase in RVP commingling approaches a maximum when the market share for the ethanol-containing gasoline becomes 30 to 50%, and declines thereafter as ethanol takes a larger market share.

Current federal law requires all gasoline sold in southern California, Sacramento, and, shortly, the San Joaquin Valley to contain an oxygenate. Under an MTBE ban, ethanol would be the only possible oxygenate with the potential for large-scale introduction. Thus, commingling would seldom happen in this large portion of California, representing 80% of the gasoline marketplace. California has requested the federal government for a waiver from the summertime oxygenate requirement to facilitate the phase-out of MTBE in these areas. If the waiver is granted, commingling will likely increase. The CaRFG3 regulations require a 0.1 psi decrease in RVP to help mitigate the effect of commingling and the Air Resources Board has committed to additional research to further quantify commingling impacts.

3.4.6. Use of Reactivity in CO-for-Evaporative Emission Trade-Offs

The approved regulations for California Phase 3 reformulated gasoline (ARB, 1999a; 1999d) allow increased evaporative VOC emissions as the oxygen content of the fuel increases above 2 wt%, reducing CO emissions. This adjustment compensates for the ozone formation potential of CO. The approved regulations use the MIR scale to make the adjustment. A recent modeling analysis (Whitten, 1999) suggests the reactivity of CO should be raised by 65%, allowing a greater increase in evaporative VOC emissions. Our review of the literature (see Appendix D) indicates the reactivity of CO is well established and regarded as having low uncertainty (Carter, 1999a). Additionally, changes to the MIR scale on which California's reactivity regulations are based should only be undertaken after careful analysis and only when the scientific evidence and the advice of the ARB Reactivity Scientific Advisory Committee warrant such a change. Our conclusion is that an increase in the assigned reactivity of CO is not justified at this time.

3.5. Mileage Penalty for Gasolines With High Ethanol Content

Increasing the oxygen content of gasoline reduces fuel economy. Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2 wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen as ethanol would likely provide less fuel economy (by ~2%) than current gasoline, while non-oxygenated CaRFG2 would improve fuel economy by ~2%. However, mass emission rates should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline with emissions measured in mass per mile, not in mass per volume of fuel.

4. Estimates of the Impact of MTBE-Free Gasolines on Future Emissions and Air Quality

One of the major recommendations of the University of California assessment of MTBE (Keller *et al.*, 1998) was to conduct modeling studies to predict the air quality concentration increases of acetaldehyde and PAN that would be expected to result from the large-scale substitution of ethanol for MTBE in the future. In order to fulfill this recommendation, we evaluated emission and air quality impacts in 2003 for the current MTBE-based CaRFG2, gasoline blended with 2.0 wt% oxygen as ethanol, gasoline blended with 3.5 wt% oxygen as ethanol, and gasoline without any oxygen. This analysis was conducted with the best available information on the emission characteristics of gasolines that will be available in 2003, and uses a comprehensive analysis of current air quality concentrations and a photochemical model with state-of-the-science chemistry to estimate air quality in the future.

4.1. Predicted Emissions for the South Coast Air Basin

The photochemical modeling analysis requires estimates of organic gas emission profiles and mass emissions of VOC, NO_x, and CO for the four 2003 fuel scenarios. Estimates are also needed for 1997 MTBE-based CaRFG2 to provide a link with baseline air quality measured during 1997. Only a summary of the derivation of emissions for evaporative and exhaust emissions is presented here. Full details are available in Appendix A.

4.1.1. Organic Gas Emission Profile Assumptions

In order to develop the emission estimates for 1997 and 2003, we developed organic gas emission profiles for each fuel and applied the profiles to all gasoline-related emission inventory categories. The emission processes for which we developed profiles include:

- Liquid gasoline.
- Hot soak and running loss evaporative.
- Diurnal and resting loss evaporative.
- Start exhaust -- catalyst and non-catalyst.
- Stabilized exhaust -- catalyst and non-catalyst.

For 1997 MTBE-based CaRFG2, we used organic gas emission profiles developed from ARB surveillance data and presented at a public workshop in September 1998 (ARB, 1998a). We used the results of a linear-programming refinery model study sponsored by the California Energy Commission (MathPro, 1999a; 1999b) to establish the liquid gasoline profiles. In general the MathPro (1999a; 1999b) study predicted significant removal of pentanes and an increased use of alkylates when MTBE is banned as a fuel oxygenate.

The liquid gasoline profiles were also applied to hot soak evaporative emissions for all the 2003 fuels as recommended from a peer review conducted by Professor Harley of the University of California at Berkeley (see Attachment A1). Running loss evaporative emissions were also speciated using the liquid gasoline profiles. Professor Harley calculated headspace vapors for all

the 2003 fuels from the liquid gasoline composition (see Attachment A1) and we applied these to diurnal and resting loss evaporative emissions for the MTBE-free scenarios.

The emission profiles for the exhaust categories were established by adjusting the profiles for the MTBE-based CaRFG2 adopted in September 1998 (ARB, 1998a). The exhaust adjustments maintain consistency with the fuel composition. The adjustments for isobutene, identified as a major byproduct of MTBE combustion in the University of California MTBE report (Koshland *et al.*, 1998), were based on analysis of results from the Auto/Oil Program (1991; 1995), the ATL (1995) study, and an ARB (1998b) study contrasting MTBE-based CaRFG2 with a non-complying ethanol-containing gasoline. In addition, we input the fuel properties into the ARB Predictive Model for exhaust emissions of benzene and 1,3-butadiene (ARB, 1995), and into newly created models for evaporative benzene emissions and exhaust emissions of acetaldehyde and formaldehyde that distinguish between MTBE and ethanol as the oxygenate (ARB, 1999b). These profiles went through several iterations and were peer reviewed by Professor Harley in June 1999 (see Attachment A1 and Appendix D), and presented at public workshops on July 12 and October 4. What is presented in Appendix A is substantially different from what was presented earlier, having been extensively revised after errors were found by the peer review of Professor Harley and during the public comment period.

4.1.2. Mass Emissions

We estimated total mass emissions of VOC, NO_x, and CO for CaRFG2 using the current mobile source emissions model, MVEI7G. Stationary source emissions were assumed to be the same for all 2003 scenarios. For the three fully complying non-MTBE gasolines, the ARB Predictive Model (ARB, 1995) constrains the total mass emissions of VOC and NO_x, so emissions of these pollutants were held constant for all the 2003 scenarios.

Based on several vehicle emission test programs (NSTC, 1997) and ambient air studies (Dolislager, 1997), CO emissions decrease with increasing fuel oxygen content. Previous ARB modeling analyses found that CO emissions have a small impact (about 10 ppb) on concentrations of ozone. We used the same motor vehicle CO inventory for the MTBE and ethanol fuel scenarios with 2.0 wt% oxygen content, and decreased the CO emissions by 7.5% for the ethanol with 3.5 wt% oxygen scenario and increased the CO emissions by 5% for the non-oxygenated scenario. Our nonlinear treatment of CO when the oxygenate is removed appears inconsistent with the findings of the NSTC (1997) that use of a 2.0 wt% oxygen wintertime gasoline results in a decrease of 10% in CO emissions. However, a substantial portion of the CO reductions that can be attributed to summertime CaRFG2 comes from properties of the fuel other than the oxygen content. This means that addition or removal of oxygen in CaRFG2 is likely to have less impact on CO emissions than from non-CaRFG2 wintertime gasolines.

We calculated emissions of benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and MTBE by applying the organic gas emission profiles to VOC mass emission estimates for gasoline-related categories (e.g., passenger cars, heavy-duty vehicles, fuel spillage, off-road mobile sources, etc.). The resulting emission inventories for the South Coast Air Basin (SoCAB) are shown in Table 4.1 to Table 4.3 for CO, NO_x, reactive organic gases (ROG), benzene, 1,3-butadiene, acetaldehyde, formaldehyde, ethanol, and MTBE. Table 4.1 summarizes the total emissions (mobile, area, stationary, and natural sources) for an average ozone episode day for the five fuel scenarios. Table 4.2 and Table 4.3 present emission changes relative to the 1997 and

2003 MTBE baselines, respectively. In comparison to the 1997 MTBE baseline inventory, emissions of all compounds (except acetaldehyde and ethanol for the ethanol-blended gasolines) are substantially reduced. Among the four 2003 scenarios, there are differences for all compounds but NO_x and ROG.

4.2. Predicted Air Quality for the South Coast Air Basin

We used photochemical modeling to predict air quality concentrations for episodic ozone conditions in 1997 and 2003, and applied these results to measured 1997 air quality during the entire year to estimate pollutant concentrations in 2003. Full details for the photochemical modeling are given in Appendix B, and Appendix C describes the air quality observed in 1997 and predicted for 2003.

4.2.1. Photochemical Model Description

We applied the Urban Airshed Model with the Flexible Chemical Mechanism interface (UAM-FCM) for the August 26 to 28, 1987 ozone episode in the SoCAB. Input files for winds, temperature, and diffusion break were developed using special air quality and meteorological data collected during the 1987 Southern California Air Quality Study (Lawson 1990; Lawson *et al.*, 1995). We simulated initial and boundary conditions, together with emission inventories for calendar years 1997 and 2003, using the meteorology from the 1987 episode. Fixing the meteorological conditions in this way allows the effects of fuel changes to be directly calculated. We used an extended version of the SAPRC-97 photochemical mechanism (Carter *et al.*, 1997) to simulate atmospheric chemical transformations. The mechanism includes explicit chemical reactions for CO, NO₂, ozone, acetaldehyde, benzene, 1,3-butadiene, ethanol, formaldehyde, HNO₃, MTBE, PAN, and PPN. The mechanism tracks secondary formation of acetaldehyde and formaldehyde separately from the contribution of direct emissions. The SAPRC-97 mechanism lumps alkylates, *n*-heptane, *n*-hexane, isobutene, toluene, and xylene isomers with similarly reacting compounds, but we did extend the mechanism to include explicit treatments of these compounds. OEHHHA determined that the maximum 1997 concentrations we provided were at least an order of magnitude below any level of concern (see Section 4.2.3.5). The UAM-FCM does not include representations of the chemical and physical processes that form particulate matter. However, PM₁₀ and PM_{2.5} concentrations are not expected to change due to the removal of MTBE from gasoline, as discussed in Section 4.2.3.2.

To establish baseline conditions, we simulated 1997 mass emissions with the organic gas emission profiles for CaRFG2. Calendar year 2003 was evaluated for CaRFG2 and the three fully complying non-MTBE gasolines. We assumed boundary conditions in 1997 and 2003 to vary from measured 1987 concentrations consistent with the emission inventory. However, initial concentrations are held constant. Model results for the first and second days of the simulation are greatly influenced by the initial conditions for ozone and its precursors. Therefore, only the results for the third day (i.e., August 28) of the simulations are reported.

Table 4.1. South Coast Air Basin Emissions (tons/day)

| Year / Scenario | CO | NO _x | ROG | Benzene | Butadiene | Acetaldehyde | Formaldehyde | Ethanol | MTBE |
|-----------------------------------|------|-----------------|------|---------|-----------|--------------|--------------|---------|-------|
| 1997 Baseline (MTBE-based CaRFG2) | 5440 | 1083 | 1037 | 17.83 | 3.46 | 6.78 | 21.71 | 33.55 | 31.15 |
| 2003 Baseline (MTBE-based CaRFG2) | 4295 | 851 | 895 | 11.82 | 2.59 | 6.00 | 18.89 | 32.10 | 21.09 |
| 2003 Ethanol at 2.0 wt% Oxygen | 4295 | 851 | 893 | 11.67 | 2.53 | 6.37 | 18.52 | 46.00 | 0.01 |
| 2003 Ethanol at 3.5 wt% Oxygen | 4052 | 851 | 894 | 11.98 | 2.55 | 7.78 | 18.41 | 53.46 | 0.01 |
| 2003 Non-Oxygenate | 4457 | 851 | 893 | 10.97 | 2.53 | 5.93 | 18.22 | 31.96 | 0.01 |

Table 4.2. Emission Changes from 1997 MTBE Baseline

| Scenario | CO | NO _x | ROG | Benzene | Butadiene | Acetaldehyde | Formaldehyde | Ethanol | MTBE |
|-----------------------------------|------|-----------------|------|---------|-----------|--------------|--------------|---------|-------|
| 2003 Baseline (MTBE-based CaRFG2) | -21% | -21% | -14% | -34% | -25% | -12% | -13% | -4% | -32% |
| 2003 Ethanol at 2.0 wt% Oxygen | -21% | -21% | -14% | -35% | -27% | -6% | -15% | 37% | -100% |
| 2003 Ethanol at 3.5 wt% Oxygen | -26% | -21% | -14% | -33% | -26% | 15% | -15% | 59% | -100% |
| 2003 Non-Oxygenate | -18% | -21% | -14% | -38% | -27% | -13% | -16% | -5% | -100% |

Table 4.3. Emission Changes from 2003 MTBE Baseline

| Scenario | CO | NO _x | ROG | Benzene | Butadiene | Acetaldehyde | Formaldehyde | Ethanol | MTBE |
|--------------------------------------|-----|-----------------|-----|---------|-----------|--------------|--------------|---------|-------|
| 2003 Ethanol Blend at 2.0 wt% Oxygen | 0% | 0% | 0% | -1% | -2% | 6% | -2% | 43% | -100% |
| 2003 Ethanol Blend at 3.5 wt% Oxygen | -6% | 0% | 0% | 1% | -1% | 30% | -3% | 67% | -100% |
| 2003 Non-Oxygenate | 4% | 0% | 0% | -7% | -2% | -1% | -4% | 0% | -100% |

4.2.2. Photochemical Model Results

We conducted two sets of model simulations. The original set of five scenarios uses our best estimates of emissions and atmospheric chemistry. An additional set of five scenarios brackets the effects of emission uncertainty and chlorine atom chemistry, uses updated MTBE and ethanol rate constants, and corrects boundary conditions for several species.

4.2.2.1. Original Model Simulations

For all five scenarios, we processed UAM-FCM results for the maximum one-hour-average, eight-hour-average (CO and ozone only), and 24-hour-average concentrations for all compounds of interest. Table 4.4 compares the changes in pollutant concentrations between the 1997 CaRFG2 base gasoline and the four 2003 fuel scenarios to give the reader a sense of temporally and spatially integrated patterns across the modeling domain. All pollutants but PPN show decreases from the 1997 baseline to the 2003 baseline (“2003 MTBE”) due to reductions in overall emissions. The predicted decreases are especially pronounced for the toxic air contaminants, ranging from 13% for population-weighted 24-hour-average formaldehyde and acetaldehyde to 33% for benzene and 43% for 1,3-butadiene. The domain maximum one-hour-average ozone is predicted to decrease 6% between 1997 and 2003. The reductions from 1997 to 2003 for the three MTBE-free scenarios are similar to the 2003 MTBE baseline for all compounds but ethanol.

Table 4.5 compares the changes in concentration between the 2003 MTBE baseline and the three 2003 MTBE-free fuel scenarios. Because fuel-related activities are the only inventoried source of MTBE, concentrations decrease 100%. Ethanol concentrations for the ethanol-blended gasoline increase by 48% (2.0 wt% oxygen) and 72% (3.5 wt% oxygen), but changes in secondary acetaldehyde from this ethanol increase are modest (0 to 2%), and total acetaldehyde is predicted to increase (4%) for only the ethanol-blended gasoline at 3.5 wt% oxygen. PAN concentrations are not predicted to increase for either ethanol-blended gasoline. Benzene concentrations increase slightly (1%) for the ethanol-blended gasoline at 3.5 wt% oxygen, with decreases predicted for the other two gasolines. All three MTBE-free gasolines produce modest reductions in 1,3-butadiene (2%) and formaldehyde (2 to 4%) concentrations and essentially no change in ozone, NO₂, nitric acid, and PPN concentrations. As expected, the non-oxygenated gasoline results in higher predicted eight-hour-average CO concentrations (3%) and the 3.5 wt% oxygen ethanol-blend in lower CO values (-9%). It should be noted that these are summertime concentrations—a time period when violations of the standard do not occur.

4.2.2.2. Upper-Bound Model Simulations

Sensitivity analysis is an evaluation of the model response to variations in one or more of the model inputs. The sensitivity simulations performed in our study bracket the cumulative effect of 1) use of EMFAC2000 instead of EMFAC7G, 2) consideration of chlorine radical chemistry, 3) use of updated rate constants for the reactions of hydroxyl radical with ethanol and MTBE, and 4) revised boundary conditions.

The on-road motor vehicle emissions were increased to evaluate the potential impact of using EMFAC2000 (ARB, 1999) instead of EMFAC7G. EMFAC2000 was not available at the time of this study, but emissions from motor vehicles increase substantially with EMFAC2000. A large increase in hydrocarbon emissions will change the NO_x-to-hydrocarbon ratio and potentially impact the radical flux. This may increase the photochemical oxidation of ethanol and lead to an increase in acetaldehyde and PAN impacts. VOC emissions were multiplied by a

factor of three to place an upper-limit to the impact of using EMFAC2000, which at one time proposed multiplication factors of 2.34 and 1.84 for the 2000 on-road motor vehicle emission inventory in the South Coast Air Basin for VOCs and NO_x, respectively. The factor of three is also consistent with an independent fuel-based inventory for the South Coast Air Basin in 1997 which proposes a multiplication factor of 3.5 ± 0.6 for on-road motor vehicle hydrocarbon emissions of stabilized exhaust (Singer and Harley, 2000). The Singer and Harley (2000) fuel-based inventory is for stabilized exhaust emissions and does not include cold start or evaporative emissions, so it is not necessarily inconsistent with draft versions of EMFAC2000. We also have some concerns with Singer and Harley's methodology (primarily lack of freeway measurements where gm/gallon emission rates are likely to be lower) and view it as an upper-bound estimate. The motor vehicle CO emissions were also increased by a factor of three to represent the impact of using EMFAC2000, which proposes a significant (a factor of about three) increase of motor vehicle CO emissions.

In response to peer review comments provided by Professor Barbara Finlayson-Pitts (see Section D-1.2 in Appendix D), the chemical mechanism was modified to include chlorine (Cl) radical chemistry as described in Section 2.1.5. A proper representation would include reactions of Cl radical with all VOCs, including methane, 1,3-butadiene, isoprene, MTBE, ethanol, benzene, and their reaction products (for example, see Fantechi *et al.*, 1998), and reactions with other inorganic species. Hence, the addition of Cl radical reactions require a revision of the atmospheric chemical mechanism, which is outside the scope of this study. In addition, there are significant uncertainties in the reliability of Cl chemistry mechanisms because of limited smog chamber data for model testing (Carter, 1999b). A method to bracket the potential impact of adding Cl radical reactions is to focus on its effect on ethanol. We added a Cl radical reaction with ethanol, assuming the same lumped products as with the OH reaction with ethanol in the SAPRC97 chemical mechanism and using a reaction rate constant of $9.4 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Two additional assumptions were made to place an upper-limit on the potential effect of including the Cl radical reaction with ethanol. First, the reaction was assumed to occur throughout the entire day and, second, we assumed a constant Cl radical concentration of $10^4 \text{ atom cm}^{-3}$ (Fantechi *et al.*, 1998) throughout the modeling domain. These Cl radical concentrations bracket the actual levels, which presumably occur only during the day and near coastal areas. Thus, the overall impact will be to greatly increase the oxidation of ethanol to acetaldehyde and PAN. The maximum impact will be for the 2003 Et3.5% scenario because of the higher ethanol emission rates in the inventory relative to the other scenarios.

In response to additional peer review comments (see Section D.1 of Appendix D), we increased the OH + ethanol rate constant by 0.03% and the OH + MTBE rate constant by 3.8%. The use of the revised kinetic rate constants will slightly increase the photochemical oxidation of ethanol and MTBE. We also revised the HONO, N₂O₅, and NO₃ boundary and region top concentrations in response to peer review comments.

**Table 4.4. Changes in Gridded Region Model Results from 1997 MTBE Baseline for
Original Simulations**

| Compound | Parameter | 2003 MTBE | 2003 Et2.0% | 2003 Et3.5% | 2003 NonOxy |
|--------------------------|-----------|-----------|-------------|-------------|-------------|
| Acetaldehyde (Total) | 1hr | -5% | -4% | -3% | -4% |
| Acetaldehyde (Total) | Daily | 0% | 0% | 0% | 0% |
| Acetaldehyde (Total) | PW | -13% | -13% | -10% | -14% |
| Acetaldehyde (Primary) | PW | -25% | -23% | 4% | -26% |
| Acetaldehyde (Secondary) | PW | -12% | -12% | -11% | -13% |
| Benzene | 1hr* | -36% | -36% | -36% | -36% |
| Benzene | Daily* | -29% | -32% | -29% | -33% |
| Benzene | PW | -33% | -34% | -32% | -36% |
| 1,3-Butadiene | 1hr | -50% | -50% | -50% | -50% |
| 1,3-Butadiene | Daily | -60% | -60% | -60% | -60% |
| 1,3-Butadiene | PW | -43% | -45% | -44% | -45% |
| CO | 1hr* | -14% | -14% | -20% | -13% |
| CO | 8hr* | -18% | -18% | -23% | -16% |
| CO | PW | -18% | -18% | -24% | -16% |
| Ethanol | 1hr* | -6% | 34% | 53% | -6% |
| Ethanol | Daily* | -5% | 39% | 59% | -5% |
| Ethanol | PW | -5% | 40% | 63% | -5% |
| Formaldehyde (Total) | 1hr | 1% | 0% | 1% | 0% |
| Formaldehyde (Total) | Daily | -13% | -16% | -14% | -16% |
| Formaldehyde (Total) | PW | -13% | -16% | -14% | -17% |
| Formaldehyde (Primary) | PW | -25% | -27% | -27% | -27% |
| Formaldehyde (Secondary) | PW | -11% | -14% | -12% | -15% |
| MTBE | 1hr* | -31% | -100% | -100% | -100% |
| MTBE | Daily* | -31% | -100% | -100% | -100% |
| MTBE | PW | -34% | -100% | -100% | -100% |
| Nitric Acid | Daily | -12% | -12% | -12% | -12% |
| Nitric Acid | PW | -11% | -11% | -11% | -11% |
| NO | PW | -46% | -45% | -46% | -45% |
| NO ₂ | 1hr | -8% | -8% | -8% | -8% |
| NO ₂ | Daily | -17% | -17% | -17% | -17% |
| NO ₂ | PW | -28% | -28% | -28% | -28% |
| Ozone | 1hr | -6% | -7% | -7% | -7% |
| Ozone | 8hr | -5% | -5% | -5% | -5% |
| PAN | 1hr | -5% | -7% | -5% | -9% |
| PAN | Daily | -4% | -5% | -3% | -6% |
| PAN | PW | -4% | -4% | -3% | -6% |
| PPN | 1hr | 0% | 0% | 0% | 0% |
| PPN | Daily | -1% | 1% | -1% | 4% |
| PPN | PW | -2% | -1% | -2% | -1% |

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.5. Changes in Gridded Region Model Results from 2003 MTBE Baseline for Original Simulations

| Compound | Parameter | 2003 Et2.0% | 2003 Et3.5% | 2003 NonOxy |
|--------------------------|-----------|-------------|-------------|-------------|
| Acetaldehyde (Total) | 1hr | 1% | 2% | 1% |
| Acetaldehyde (Total) | Daily | 0% | 0% | 0% |
| Acetaldehyde (Total) | PW | 0% | 4% | -1% |
| Acetaldehyde (Primary) | PW | 4% | 39% | -1% |
| Acetaldehyde (Secondary) | PW | 0% | 2% | -1% |
| Benzene | 1hr* | 0% | 0% | 0% |
| Benzene | Daily* | -4% | 0% | -6% |
| Benzene | PW | -3% | 1% | -5% |
| 1,3-Butadiene | 1hr* | 0% | 0% | 0% |
| 1,3-Butadiene | Daily* | 0% | 0% | 0% |
| 1,3-Butadiene | PW | -2% | -2% | -2% |
| CO | 1hr* | 0% | -7% | 2% |
| CO | 8hr* | 0% | -7% | 2% |
| CO | PW | 0% | -7% | 2% |
| Ethanol | 1hr* | 43% | 63% | 0% |
| Ethanol | Daily* | 46% | 67% | 0% |
| Ethanol | PW | 48% | 72% | 0% |
| Formaldehyde (Total) | 1hr | -1% | 0% | -1% |
| Formaldehyde (Total) | Daily | -3% | -1% | -4% |
| Formaldehyde (Total) | PW | -4% | -2% | -4% |
| Formaldehyde (Primary) | PW | -3% | -3% | -4% |
| Formaldehyde (Secondary) | PW | -4% | -1% | -4% |
| MTBE | 1hr* | -100% | -100% | -100% |
| MTBE | Daily* | -100% | -100% | -100% |
| MTBE | PW | -100% | -100% | -100% |
| Nitric Acid | Daily | 0% | -1% | 0% |
| Nitric Acid | PW | 0% | 0% | 0% |
| NO | PW | 1% | 0% | 1% |
| NO ₂ | 1hr | 0% | 0% | 0% |
| NO ₂ | Daily | 0% | 0% | 0% |
| NO ₂ | PW | 0% | 0% | 0% |
| Ozone | 1hr | -1% | -1% | -1% |
| Ozone | 8hr | 0% | 0% | 0% |
| PAN | 1hr | -2% | 0% | -5% |
| PAN | Daily | -1% | 1% | -2% |
| PAN | PW | 0% | 1% | -1% |
| PPN | 1Hr | 0% | 0% | 0% |
| PPN | Daily | 2% | -1% | 4% |
| PPN | PW | 0% | -1% | 1% |

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.6. Changes in Gridded Region Model Results from 1997 MTBE Baseline for Upper-Bound Simulations

| Compound | Parameter | 2003 MTBE | 2003 Et2.0% | 2003 Et3.5% | 2003 NonOxy |
|--------------------------|-----------|-----------|-------------|-------------|-------------|
| Acetaldehyde (Total) | 1hr | -30% | -28% | -23% | -30% |
| Acetaldehyde (Total) | Daily | -28% | -26% | -22% | -27% |
| Acetaldehyde (Total) | PW | -24% | -24% | -18% | -25% |
| Acetaldehyde (Primary) | PW | -32% | -24% | 1% | -32% |
| Acetaldehyde (Secondary) | PW | -23% | -24% | -20% | -25% |
| Benzene | 1hr* | -42% | -42% | -42% | -46% |
| Benzene | Daily* | -41% | -41% | -40% | -45% |
| Benzene | PW | -43% | -44% | -42% | -47% |
| 1,3-Butadiene | 1hr | -40% | -40% | -40% | -40% |
| 1,3-Butadiene | Daily | -47% | -47% | -47% | -47% |
| 1,3-Butadiene | PW | -44% | -46% | -46% | -46% |
| CO | 1hr* | -29% | -29% | -32% | -26% |
| CO | 8hr* | -28% | -28% | -31% | -25% |
| CO | PW | -27% | -27% | -31% | -25% |
| Ethanol | 1hr* | -6% | 97% | 148% | -6% |
| Ethanol | Daily* | -5% | 93% | 145% | -6% |
| Ethanol | PW | -5% | 102% | 162% | -6% |
| Formaldehyde (Total) | 1hr | -30% | -34% | -32% | -34% |
| Formaldehyde (Total) | Daily | -30% | -34% | -32% | -35% |
| Formaldehyde (Total) | PW | -25% | -30% | -27% | -31% |
| Formaldehyde (Primary) | PW | -33% | -35% | -36% | -36% |
| Formaldehyde (Secondary) | PW | -23% | -29% | -25% | -30% |
| MTBE | 1hr* | -38% | -100% | -100% | -100% |
| MTBE | Daily* | -39% | -100% | -100% | -100% |
| MTBE | PW | -39% | -100% | -100% | -100% |
| Nitric Acid | Daily | -18% | -18% | -18% | -18% |
| Nitric Acid | PW | -15% | -14% | -15% | -14% |
| NO | PW | -41% | -40% | -40% | -39% |
| NO ₂ | 1hr | -19% | -19% | -19% | -19% |
| NO ₂ | Daily | -19% | -19% | -19% | -19% |
| NO ₂ | PW | -26% | -26% | -26% | -26% |
| Ozone | 1hr | -22% | -25% | -24% | -25% |
| Ozone | 8hr | -20% | -23% | -21% | -23% |
| PAN | 1hr | -37% | -40% | -35% | -43% |
| PAN | Daily | -33% | -36% | -33% | -37% |
| PAN | PW | -29% | -31% | -27% | -32% |
| PPN | 1hr | -35% | -35% | -37% | -33% |
| PPN | Daily | -33% | -34% | -35% | -34% |
| PPN | PW | -27% | -28% | -29% | -27% |

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.7. Changes in Gridded Region Model Results from 2003 MTBE Baseline for Upper-Bound Simulations

| Compound | Parameter | 2003 Et2.0% | 2003 Et3.5% | 2003 NonOxy |
|--------------------------|-----------|-------------|-------------|-------------|
| Acetaldehyde (Total) | 1hr | 2% | 10% | -1% |
| Acetaldehyde (Total) | Daily | 2% | 7% | 0% |
| Acetaldehyde (Total) | PW | 0% | 7% | -2% |
| Acetaldehyde (Primary) | PW | 11% | 49% | -1% |
| Acetaldehyde (Secondary) | PW | -1% | 4% | -2% |
| Benzene | 1hr* | 0% | 0% | -7% |
| Benzene | Daily* | -1% | 1% | -7% |
| Benzene | PW | -1% | 1% | -7% |
| 1,3-Butadiene | 1hr* | 0% | 0% | 0% |
| 1,3-Butadiene | Daily* | 0% | 0% | 0% |
| 1,3-Butadiene | PW | -3% | -3% | -3% |
| CO | 1hr* | 0% | -5% | 4% |
| CO | 8hr* | 0% | -5% | 3% |
| CO | PW | 0% | -5% | 3% |
| Ethanol | 1hr* | 110% | 166% | 0% |
| Ethanol | Daily* | 104% | 159% | -1% |
| Ethanol | PW | 113% | 177% | -1% |
| Formaldehyde (Total) | 1hr | -5% | -2% | -6% |
| Formaldehyde (Total) | Daily | -6% | -2% | -7% |
| Formaldehyde (Total) | PW | -6% | -3% | -8% |
| Formaldehyde (Primary) | PW | -3% | -4% | -5% |
| Formaldehyde (Secondary) | PW | -7% | -2% | -8% |
| MTBE | 1hr* | -100% | -100% | -100% |
| MTBE | Daily* | -100% | -100% | -100% |
| MTBE | PW | -100% | -100% | -100% |
| Nitric Acid | Daily | -1% | -1% | -1% |
| Nitric Acid | PW | 1% | 0% | 1% |
| NO | PW | 2% | 1% | 3% |
| NO ₂ | 1hr | 0% | 0% | 0% |
| NO ₂ | Daily | -1% | 0% | -1% |
| NO ₂ | PW | 0% | 0% | 0% |
| Ozone | 1hr | -4% | -2% | -4% |
| Ozone | 8hr | -3% | -2% | -3% |
| PAN | 1hr | -4% | 3% | -9% |
| PAN | Daily | -4% | 1% | -6% |
| PAN | PW | -3% | 1% | -5% |
| PPN | 1Hr | 0% | -3% | 3% |
| PPN | Daily | -2% | -3% | -1% |
| PPN | PW | -2% | -2% | 0% |

1hr, 8hr, Daily, and PW are gridded region maximum 1hr, 8hr, daily hour averages, and population weighted summer daily average, respectively.

*=Data represent changes for grid cell containing Lynwood (location of highest estimated 1997 concentration).

Table 4.6 compares the changes in pollutant concentrations between the 1997 CaRFG2 base gasoline and the four 2003 fuel scenarios, while Table 4.7 compares the three 2003 MTBE-free fuel scenarios with the 2003 MTBE. The predicted domain maximum one-hour-average concentrations (see Table 5.3 in Appendix B) increase significantly for many species when the motor vehicle VOC emissions were increased by a factor of three. The major finding is that the predicted maximum one-hour-average concentrations for acetaldehyde and PAN from the ethanol-containing gasoline (Et3.5%) are now 1.4 ppb and 1.3 ppb, respectively, greater than the maximum predicted for the non-oxygenated gasoline (NonOxy). These acetaldehyde and PAN impacts from the ethanol-containing gasoline represent an upper limit because the factor of three increase in all on-road hydrocarbon emissions is larger than expected from EMFAC2000 when it becomes final, the assumed Cl radical concentrations are likely very high for inland areas, and the ozone episode modeled here is an extreme ozone event.

In addition to the three-dimensional airshed model simulations, we also investigated the ozone, PAN, and PPN (which includes higher molecular weight acyl peroxy nitrates) formation potentials for each of the explicit VOCs and lumped species in the SAPRC-97 chemical mechanism. This was used primarily to explain the lack of sensitivity of PAN formation to the ethanol content of the gasoline. We implemented the SAPRC-97 chemical mechanism in a box model with observed air quality for ten scenarios spanning the past three decades in southern California, and two cases in Brazil with widespread use of ethanol. As described in Appendix B, the box model simulations are consistent with the results from the three-dimensional airshed model that other VOCs, (that is, aromatic compounds, olefins) not ethanol, are primarily responsible for PAN formation.

4.2.3. Current and Future Air Quality

In order to perform a health-risk analysis, OEHHA requested maximum 1997 and 2003 population-weighted annual-average, maximum 24-hour-average, and maximum one-hour-average concentrations for the toxic air contaminants and fuel oxygenates, and concentrations for the appropriate averaging times for the criteria air pollutants (including PAN and PPN). Analyses were only done for the SoCAB, the most populated and most polluted air basin in California. This is also the area in California (and perhaps the world) with the most air quality data, speciated VOCs and toxic air contaminants in particular. Ambient air quality data for criteria pollutants in 1996-1998 were used to represent the 1997 baseline to account for natural year-to-year meteorological fluctuations. Only 1996-1997 toxics data were used to represent the 1997 baseline since 1998 data were not readily available at the time of the analysis. Data from before 1996 were not used because fuels used then did not satisfy the CaRFG2 requirements. We used data from the following sources:

- 1996-1998 Criteria Pollutant Monitoring Network in the SoCAB.
- 1996-1997 ARB Toxic Air Contaminant Network in the SoCAB (“TAC data”).
- 1996 SoCAB VOC Monitoring Study by Desert Research Institute (“DRI data”).
- 1996 Desert Research Institute Sepulveda Tunnel Study.
- 1996 and 1997 UC Berkeley Caldecott Tunnel Studies.
- 1997 ARB Emission Inventory for the SoCAB.

Data from the 1997 Southern California Ozone Study (SCOS97-NARSTO) and Multiple Air Toxics Exposure Study (MATES) II data were not readily available at the time of our analysis. Although we originally proposed to include data from a 1999 UC Berkeley Tunnel Study conducted in July, these data were also not available at the time of our analysis.

The photochemical modeling results were used to establish future air quality concentrations. For estimating future maximum one-hour-average and 24-hour-average concentrations, we used the maximum concentrations in the gridded modeling region for the third day of the model simulation. For the population-weighted annual-average exposure estimates, we used the region-wide population-weighted average of the daily-average model results. Results for the original and upper-bound modeling simulations are given in Table 4.8 and Table 4.9, respectively. The “upper baseline” and “lower baseline” in the tables reflect different assumptions of 1997 air quality due to incomplete measurements. For pollutants with more complete data (e.g., carbon monoxide, ozone), only a “best baseline” is given.

4.2.3.1. Acetaldehyde, Benzene, 1,3-Butadiene, and Formaldehyde

We used two different approaches to estimate 1997 benzene and 1,3-butadiene concentrations. First, we used measured concentrations directly from the TAC sampling network. In addition, we used least-squares linear regression (forced through the origin after accounting for background concentration) to develop ratios between these toxic air contaminants and CO. We found good correlations with CO for benzene and 1,3-butadiene. We used the regression results to estimate concentrations at locations where there are no direct TAC measurements, but there are CO measurements. The latter approach allowed us to estimate pollutant concentrations at nineteen locations, rather than the five locations for which toxics sampling data are available. Model results for benzene and 1,3-butadiene were used to extrapolate from the 1997 base year to the various 2003 scenarios. The range of estimates developed using the different approaches is given in Table 4.8.

We considered three different approaches to estimate 1997 acetaldehyde and formaldehyde concentrations. First, we used measured concentrations directly from the toxics sampling network. Second, to derive maximum one-hour-average concentrations from 24-hour-average measurements, we used the corresponding ratio for ozone. Third, we attempted to develop relationships between aldehydes and both CO and total oxidant (sum of ozone and NO_2) so aldehyde values could be estimated at many more locations than are sampled with the TAC monitoring network. Our attempt to correlate aldehydes with CO and oxidant was not considered sufficiently reliable and was abandoned.

Future year maximum one-hour and daily acetaldehyde and formaldehyde estimates were extrapolated from 1997 using modeled results for total acetaldehyde and total formaldehyde. To estimate future year population-weighted exposure, we first split 1997 estimates into primary and secondary components and then applied model results to extrapolate each component separately. The separate components were then added to obtain total acetaldehyde and total formaldehyde. Table 4.8 reports the range of estimates developed using all except the correlation method.

**Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin
Using Original Model Simulations**

| Pollutant / Avg. Type | Estimate Type | Year / Scenario | | | | |
|---------------------------|--|-----------------|------|--------|--------|--------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| | | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| Benzene, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 22.4 | 14.3 | 14.3 | 14.3 | 14.3 |
| | Lower Baseline | 11.6 | 7.4 | 7.4 | 7.4 | 7.4 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 9.5 | 6.8 | 6.5 | 6.8 | 6.4 |
| | Lower Baseline | 7.4 | 5.3 | 5.1 | 5.3 | 4.9 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper Baseline | 1.19 | 0.80 | 0.78 | 0.81 | 0.76 |
| | Lower Baseline | 1.07 | 0.72 | 0.70 | 0.73 | 0.69 |
| 1,3-Butadiene, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 6.7 | 3.4 | 3.4 | 3.4 | 3.4 |
| | Lower Baseline | 3.1 | 1.6 | 1.6 | 1.6 | 1.6 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 2.9 | 1.2 | 1.2 | 1.2 | 1.2 |
| | Lower Baseline | 2.0 | 0.8 | 0.8 | 0.8 | 0.8 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper Baseline | 0.36 | 0.20 | 0.20 | 0.20 | 0.20 |
| | Lower Baseline | 0.34 | 0.19 | 0.19 | 0.19 | 0.19 |
| Acetaldehyde, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 17.7 | 16.7 | 16.9 | 17.1 | 16.9 |
| | Lower Baseline | 13.8 | 13.1 | 13.2 | 13.4 | 13.2 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 6.2 | 6.2 | 6.2 | 6.2 | 6.2 |
| | Lower Baseline | 5.1 | 5.1 | 5.1 | 5.1 | 5.1 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper | 1.8 | 1.6 | 1.6 | 1.8 | 1.6 |
| | Lower | 1.8 | 1.5 | 1.6 | 1.7 | 1.5 |

**Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin
Using Original Model Simulations-continued**

| | | Year / Scenario | | | | |
|-----------------------|-------------------------------------|-----------------|---|--------|--------|-------------------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| Pollutant / Avg. Type | Estimate Type | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| Formaldehyde, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 37.8 | 38.3 | 37.8 | 38.1 | 37.8 |
| | Lower Baseline | 20.3 | 20.6 | 20.3 | 20.5 | 20.3 |
| | Maximum Daily Average | | | | | |
| | Best Baseline | 14.0 | 12.2 | 11.8 | 12.1 | 11.7 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper | 4.7 | 4.2 | 4.1 | 4.1 | 4.0 |
| | Lower | 4.7 | 4.1 | 4.0 | 4.0 | 4.0 |
| Carbon Monoxide, ppm | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Best Baseline | 22.5 | 19.2 | 19.2 | 18.0 | 19.7 ^a |
| | Maximum 8-Hour Average | | | | | |
| | Best Baseline | 17.5 | 14.3 | 14.3 | 13.4 | 14.7 ^a |
| Nitrogen Dioxide, ppm | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Best Baseline | 0.255 | 0.235 | 0.235 | 0.235 | 0.235 |
| | Maximum Daily Average | | | | | |
| | Best Baseline | 0.117 | 0.098 | 0.097 | 0.097 | 0.097 |
| | Maximum Annual Average | | | | | |
| | Best Baseline | 0.043 | No significant difference expected among 2003 scenarios | | | |
| Ozone, ppm | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Best Baseline | 0.244 | 0.230 | 0.228 | 0.228 | 0.228 |
| | Maximum 8-Hour Average | | | | | |
| | Best Baseline | 0.206 | 0.196 | 0.196 | 0.196 | 0.196 |

^aThis apparent increase is a function of the emission assumptions. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

**Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin
Using Original Model Simulations-continued**

| | | Year / Scenario | | | | | |
|--|-------------------------------------|-----------------|---|--------|--------|--------|---|
| | | 1997 | 2003 | 2003 | 2003 | 2003 | |
| Pollutant / Avg. Type | Estimate Type | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy | |
| Particulate Matter (10 μm or less), μg/m ³ | | | | | | | |
| Maximum Daily Average | | | | | | | |
| | Best Baseline | 227 | No difference expected among 2003 scenarios | | | | |
| Maximum Annual Geometric Mean | | | | | | | |
| | Best Baseline | 56 | No difference expected among 2003 scenarios | | | | |
| Particulate Matter (2.5 μm or less), μg/m ³ | | | | | | | |
| Maximum Daily Average | | | | | | | |
| | Best Baseline | 81 | No difference expected among 2003 scenarios | | | | |
| Maximum Annual Average | | | | | | | |
| | Best Baseline | 25.9 | No difference expected among 2003 scenarios | | | | |
| Ethanol, ppb (Estimated from Summer Measurements) | | | | | | | |
| Maximum 1-Hour Average | | | | | | | |
| | Upper Baseline | 108 | 101 | 145 | 165 | 101 | |
| | Lower Baseline | 78 | 74 | 114 | 140 | 74 | |
| Maximum Daily Average | | | | | | | |
| | Upper Baseline | 51 | 49 | 71 | 81 | 49 | |
| | Lower Baseline | 47 | 45 | 64 | 75 | 45 | |
| Population-Weighted Annual Exposure | | | | | | | |
| | Upper Baseline | 5.4 | 5.1 | 7.6 | 8.8 | 5.1 | |
| MTBE, ppb | | | | | | | |
| | Maximum 1-Hour Average | | | | | | |
| | | Upper Baseline | 67 | 46 | 0 | 0 | 0 |
| | | Lower Baseline | 19 | 13 | 0 | 0 | 0 |
| | Maximum Daily Average | | | | | | |
| | | Upper Baseline | 29 | 20 | 0 | 0 | 0 |
| | | Lower Baseline | 13 | 9 | 0 | 0 | 0 |
| | Population-Weighted Annual Exposure | | | | | | |
| | | Upper Baseline | 3.9 | 2.6 | 0 | 0 | 0 |
| | | Lower Baseline | 3.6 | 2.4 | 0 | 0 | 0 |

Table 4.8. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Original Model Simulations-continued

| Pollutant / Avg. Type | Estimate Type | Year / Scenario | | | | |
|---|--|-----------------|------|--------|--------|--------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| | | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| PAN, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 10.0 | 9.5 | 9.3 | 9.5 | 9.1 |
| | Lower Baseline | 5.0 | 4.8 | 4.7 | 4.8 | 4.5 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 5.0 | 4.8 | 4.8 | 4.9 | 4.7 |
| | Lower Baseline | 2.5 | 2.4 | 2.4 | 2.4 | 2.4 |
| PPN^a, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| | Lower Baseline | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 2.0 | 2.0 | 2.0 | 2.0 | 2.1 |
| | Lower Baseline | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Nitric Acid, ppb (Model Output Only) | | | | | | |
| | Maximum Daily Average | | | | | |
| | Model | 36.7 | 32.4 | 32.3 | 32.2 | 32.3 |
| | Population-Weighted Summer Daily Exposure | | | | | |
| | Model | 12.4 | 11.0 | 11.0 | 11.0 | 11.0 |

^aPPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates.

4.2.3.2. CO, NO₂, Ozone, PM₁₀, and PM_{2.5}

For CO, NO₂, ozone, PM₁₀, and PM_{2.5}, we used maximum concentrations observed in 1996-1998 to represent the 1997 baseline and scaled them to 2003 with the photochemical modeling results. The predicted concentrations for the 1997 MTBE baseline, the 2003 MTBE baseline, the 2.0 wt% oxygen content ethanol-blended gasoline ("Et2.0%"), the 3.5 wt% oxygen content ethanol-blended gasoline ("Et3.5%"), and the non-oxygenated gasoline ("NonOxy") are reported in Table 4.8. The apparent CO increase is a function of the emission assumptions for summertime conditions applied to the winter, when CO concentrations exceed the state and national ambient air quality standards. Due to the wintertime oxygenate requirement for the SoCAB, CO concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

We conducted a qualitative analysis for particulate matter. $PM_{2.5}$ can be approximated as the sum of nitrates, sulfates, organic carbon, elemental carbon, and secondary organic carbon. PM_{10} is roughly the sum of $PM_{2.5}$ and coarse dust. Gasoline-fueled motor vehicles are a relatively small contributor to sulfates and elemental carbon in the SoCAB and emissions of these compounds are not expected to be a function of the fuel oxygenate. Nitrates and organic carbon are not expected to change because NO_x and VOC emissions are fixed. The maximum 24-hour-average concentration for HNO_3 , the main nitrate precursor, decreases by 11% from 1997 to 2003, and does not change among the 2003 fuel scenarios. Odum *et al.* (1997) concluded that the aromatic content of fuels is primarily responsible for forming secondary organic aerosols. Since there was very little variation in aromatic content among the fuels, PM_{10} and $PM_{2.5}$ concentrations are not expected to change appreciably as a result of the introduction of MTBE-free gasolines. Vehicle activity is not likely to vary with the fuel, so coarse dust can be assumed to be constant as well. Therefore, the removal of MTBE is not expected to have an impact on PM_{10} and $PM_{2.5}$ concentrations.

4.2.3.3. Ethanol and MTBE

The only ethanol air quality data readily available were those collected by DRI in the summers of 1995 and 1996. We used the 1996 data as the basis for estimating representative concentrations for 1997. The highest ethanol concentrations are expected in winter. Given only summer data, it was challenging to estimate concentrations for a different season. We opted to use CO as an index of mixing and dispersion to extrapolate from measured maximum ethanol concentrations in the summer to a different season. Similar to other pollutants, we attempted to correlate ethanol with CO, but results were poor. This was not surprising, given that on-road vehicles currently emit less than 1% of the estimated ethanol emissions in the SoCAB.

We used the two approaches described above for benzene and 1,3-butadiene to estimate MTBE concentrations. We found good correlations with CO for some data sets and not others. Range in estimates for ethanol and MTBE are given in Table 4.8.

4.2.3.4. PAN and PPN

Grosjean (1999b) analyzed prior measurement programs for PAN and PPN. They have no direct sources and form *in situ* in the atmosphere. PAN has been measured earlier and more frequently in the SoCAB than anywhere else in the world (about 25 studies that span some 35 years). The highest PAN concentrations were recorded during early studies (and often outside the summer ozone season), e.g., 60 to 65 ppb in the late 1960s. Many of the subsequent studies lasted only a few days, weeks, or months, thus providing us with no consistent basis to assess long-term trends. High concentrations of PAN (40 ppb or more) have been recorded until about 1980, and concentrations of PAN appear to have decreased substantially thereafter. No PAN concentration higher than 10 ppb has been reported since 1991. Consistent with the downward trend observed for maximum one-hour-average PAN concentrations, 24-hour-average PAN concentrations have declined from 15 to 20 ppb in the late 1960s and until 1980, to 5 to 12 ppb in the late 1980s, and 2 to 5 ppb in 1993.

Seasonal variations of PAN are sparsely documented, especially so in the last decade (no data since 1987). Results from earlier studies indicate that high concentrations of PAN were often recorded outside of the traditional smog season, and that the coastal and central regions of the SoCAB may experience higher concentrations of PAN during the late fall than during the summer months. However, even though PAN has not been monitored routinely over a long

Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Upper-Bound Model Simulations

| Pollutant / Avg. Type | Estimate Type | Year / Scenario | | | | |
|---------------------------|--|-----------------|------|--------|--------|--------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| | | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| Benzene, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 22.4 | 13.1 | 13.1 | 13.1 | 12.1 |
| | Lower Baseline | 11.6 | 6.8 | 6.8 | 6.8 | 6.3 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 9.5 | 5.6 | 5.6 | 5.7 | 5.2 |
| | Lower Baseline | 7.4 | 4.4 | 4.3 | 4.4 | 4.1 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper Baseline | 1.19 | 0.68 | 0.67 | 0.69 | 0.63 |
| | Lower Baseline | 1.07 | 0.61 | 0.60 | 0.62 | 0.57 |
| 1,3-Butadiene, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 6.7 | 4.0 | 4.0 | 4.0 | 4.0 |
| | Lower Baseline | 3.1 | 1.9 | 1.9 | 1.9 | 1.9 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 2.9 | 1.5 | 1.5 | 1.5 | 1.5 |
| | Lower Baseline | 2.0 | 1.1 | 1.1 | 1.1 | 1.1 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper Baseline | 0.36 | 0.20 | 0.19 | 0.20 | 0.20 |
| | Lower Baseline | 0.34 | 0.19 | 0.18 | 0.19 | 0.18 |
| Acetaldehyde, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 17.7 | 12.4 | 12.7 | 13.6 | 12.3 |
| | Lower Baseline | 13.8 | 9.7 | 9.9 | 10.6 | 9.6 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 11.0 | 7.9 | 8.1 | 8.5 | 8.0 |
| | Lower Baseline | 5.1 | 3.7 | 3.8 | 4.0 | 3.7 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper | 1.8 | 1.5 | 1.5 | 1.8 | 1.5 |
| | Lower | 1.8 | 1.4 | 1.5 | 1.7 | 1.4 |

**Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin
Using Upper-Bound Model Simulations-continued**

| | | Year / Scenario | | | | |
|-----------------------|-------------------------------------|-----------------|---|--------|--------|--------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| Pollutant / Avg. Type | Estimate Type | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| Formaldehyde, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 37.8 | 26.5 | 25.1 | 25.9 | 24.9 |
| | Lower Baseline | 20.3 | 14.2 | 13.5 | 13.9 | 13.4 |
| | Maximum Daily Average | | | | | |
| | Best Baseline | 14.0 | 9.8 | 9.2 | 9.6 | 9.1 |
| | Population-Weighted Annual Exposure | | | | | |
| | Upper | 4.7 | 3.7 | 3.4 | 3.5 | 3.4 |
| | Lower | 4.7 | 3.6 | 3.4 | 3.5 | 3.4 |
| Carbon Monoxide, ppm | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Best Baseline | 22.5 | 16.1 | 16.1 | 15.3 | 16.6 |
| | Maximum 8-Hour Average | | | | | |
| | Best Baseline | 17.5 | 12.7 | 12.7 | 12.1 | 13.1 |
| Nitrogen Dioxide, ppm | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Best Baseline | 0.255 | 0.207 | 0.207 | 0.207 | 0.207 |
| | Maximum Daily Average | | | | | |
| | Best Baseline | 0.117 | 0.095 | 0.095 | 0.095 | 0.095 |
| | Maximum Annual Average | | | | | |
| | Best Baseline | 0.043 | No difference expected among 2003 scenarios | | | |
| Ozone, ppm | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Best Baseline | 0.244 | 0.190 | 0.182 | 0.186 | 0.182 |
| | Maximum 8-Hour Average | | | | | |
| | Best Baseline | 0.206 | 0.165 | 0.159 | 0.162 | 0.159 |

^aThis apparent increase is a function of the emission assumptions. Due to the wintertime oxygenate requirement for the South Coast Air Basin, carbon monoxide concentrations within the nonattainment area of Los Angeles County will not differ from the 2003 MTBE baseline.

**Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin
Using Upper-Bound Model Simulations-continued**

| | | Year / Scenario | | | | |
|--|----------------|-----------------|---|--------|--------|--------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| Pollutant / Avg. Type | Estimate Type | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| Particulate Matter (10 μm or less), μg/m ³ | | | | | | |
| Maximum Daily Average | | | | | | |
| | Best Baseline | 227 | No difference expected among 2003 scenarios | | | |
| Maximum Annual Geometric Mean | | | | | | |
| | Best Baseline | 56 | No difference expected among 2003 scenarios | | | |
| Particulate Matter (2.5 μm or less), μg/m ³ | | | | | | |
| Maximum Daily Average | | | | | | |
| | Best Baseline | 81 | No difference expected among 2003 scenarios | | | |
| Maximum Annual Average | | | | | | |
| | Best Baseline | 25.9 | No difference expected among 2003 scenarios | | | |
| Ethanol, ppb (Estimated from Summer Measurements) | | | | | | |
| Maximum 1-Hour Average | | | | | | |
| | Upper Baseline | 108 | 101 | 213 | 268 | 101 |
| | Lower Baseline | 78 | 74 | 191 | 267 | 74 |
| Maximum Daily Average | | | | | | |
| | Upper Baseline | 51 | 48 | 98 | 125 | 48 |
| | Lower Baseline | 47 | 45 | 93 | 121 | 44 |
| Population-Weighted Annual Exposure | | | | | | |
| | Upper Baseline | 5.4 | 5.1 | 10.9 | 14.2 | 5.1 |
| MTBE, ppb | | | | | | |
| Maximum 1-Hour Average | | | | | | |
| | Upper Baseline | 67 | 41 | 0 | 0 | 0 |
| | Lower Baseline | 19 | 12 | 0 | 0 | 0 |
| Maximum Daily Average | | | | | | |
| | Upper Baseline | 29 | 18 | 0 | 0 | 0 |
| | Lower Baseline | 13 | 8 | 0 | 0 | 0 |
| Population-Weighted Annual Exposure | | | | | | |
| | Upper Baseline | 3.9 | 2.4 | 0 | 0 | 0 |
| | Lower Baseline | 3.6 | 2.2 | 0 | 0 | 0 |

Table 4.9. Range of Predicted 1997 and 2003 Air Quality for the South Coast Air Basin Using Upper-Bound Model Simulations -continued

| Pollutant / Avg. Type | Estimate Type | Year / Scenario | | | | |
|---|--|-----------------|------|--------|--------|--------|
| | | 1997 | 2003 | 2003 | 2003 | 2003 |
| | | MTBE | MTBE | Et2.0% | Et3.5% | NonOxy |
| PAN, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 10.0 | 6.3 | 6.0 | 6.5 | 5.7 |
| | Lower Baseline | 5.0 | 3.1 | 3.0 | 3.2 | 2.9 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 5.0 | 3.3 | 3.2 | 3.4 | 3.1 |
| | Lower Baseline | 2.5 | 1.7 | 1.6 | 1.7 | 1.6 |
| PPN^a, ppb | | | | | | |
| | Maximum 1-Hour Average | | | | | |
| | Upper Baseline | 3.0 | 1.9 | 1.9 | 1.9 | 2.0 |
| | Lower Baseline | 1.5 | 1.0 | 1.0 | 0.9 | 1.0 |
| | Maximum Daily Average | | | | | |
| | Upper Baseline | 2.0 | 1.3 | 1.3 | 1.3 | 1.3 |
| | Lower Baseline | 1.0 | 0.7 | 0.7 | 0.7 | 0.7 |
| Nitric Acid, ppb (Model Output Only) | | | | | | |
| | Maximum Daily Average | | | | | |
| | Model | 39.9 | 32.8 | 32.6 | 32.6 | 32.7 |
| | Population-Weighted Summer Daily Exposure | | | | | |
| | Model | 12.4 | 10.6 | 10.6 | 10.6 | 10.6 |

^aPPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates.

period, many special studies demonstrate a downwind trend on average. Ozone data can be used to predict the time of maximum PAN but not to estimate PAN concentrations and their diurnal, seasonal, and spatial variations. It appears that thermal decomposition of PAN may account for much of the differences between diurnal, spatial, and seasonal variations of ambient PAN and those of ambient ozone. A wide range of estimates for PAN concentrations is given in Table 4.8.

Even less information is available for PPN than for PAN. Ambient concentrations of PPN have been reported in only nine studies. The highest concentrations of PPN were up to 5 to 6 ppb in earlier studies and 1 ppb or less in recent years. Twenty-four-hour-average concentrations range from 0.1 to 1.8 ppb. There are no data on seasonal variations or annual averages. Diurnal variations of ambient PPN are closely related to those of PAN. The slopes of

the linear regressions of ambient PPN versus ambient PAN at all locations studied in 1993 and 1997 range from 0.10 to 0.17 (average = 0.15). These values may serve as a baseline when using the PPN-to-PAN concentration ratio as an indicator of the possible impact of replacing MTBE by ethanol on future PAN air quality in the SoCAB. A wide range of estimates for PPN concentrations is given in Table 4.8.

4.2.3.5. Alkylates, *n*-Heptane, *n*-Hexane, Isobutene, Toluene, and Xylene Isomers

OEHHA requested information on maximum annual-average and maximum one-hour-average concentrations for alkylates, *n*-heptane, *n*-hexane, isobutene, toluene, and xylene isomers. We provided estimates in Table 4.10 by developing ratios between these compounds and CO using the techniques described in Section 4.2.3.1. In general, we observed good correlation with CO for all compounds for all but a few datasets. OEHHA later concluded that there is no indication of a toxicological problem with any of the alkylates, primarily due to lack of data. The maximum concentrations for *n*-heptane, *n*-hexane, isobutene, toluene, and xylene isomers are at least an order of magnitude below any level of concern, so there was no need to establish 2003 concentrations (which require photochemical modeling).

Table 4.10. Estimated 1997 Maximum Toxic Concentrations

| Compound | One-Hour Average (ppb) | Annual Average (ppb) |
|-----------------------------|------------------------|----------------------|
| Total Alkylates | 146-216 | 15.6-23.0 |
| <i>n</i> -Heptane | 2-7 | 0.2-0.7 |
| <i>n</i> -Hexane | 11-22 | 1.2-2.4 |
| Isobutene | 20-36 | 2.2-3.8 |
| Toluene | 52-103 | 6-11 |
| <i>m</i> & <i>p</i> -Xylene | 25-43 | 2.6-4.6 |
| <i>o</i> -Xylene | 9-40 | 1.0-4.3 |

4.3. Air Quality Impacts for Other Areas of California

Primarily due to the lack of ambient air quality measurements for many of the air contaminants of concern, we were unable to predict air quality for other areas of California. However, our analysis for the South Coast Air Basin can be considered the worst-case situation in comparison to other air basins. It has the highest baseline air quality concentrations, the conditions most conducive to formation of secondary air pollutants (e.g., ozone, acetaldehyde, PAN), the most emissions, and the highest number of gasoline-related emission sources in California. For most of the directly emitted air pollutants, the predicted air quality impacts are roughly equal to the emission impacts (as shown in Table 4.11 and Table 4.12). This is especially true for the comparison to the 2003 MTBE baseline (Table 4.12). Once EMFAC2000 becomes available, it will be relatively straightforward to estimate the emission impacts of the MTBE-free fuels and we can safely infer that the air quality impacts will be similar. Since the air quality impacts for the secondary air pollutants were modest for the high photochemistry episode that was modeled, we can safely assume that impacts for these pollutants in other air basins will be even smaller.

Table 4.11. Comparison of Emission and Modeled Air Quality Changes from 1997 MTBE Baseline

| Scenario / Type of Change | CO | NO _x (NO ₂) | NO _x (HNO ₃) | Benzene | Butadiene | Acetaldehyde (Primary) | Formaldehyde (Primary) | Ethanol | MTBE |
|--|------|---------------------------------------|--|---------|-----------|---------------------------|---------------------------|---------|-------|
| 2003 Baseline Inventory (MTBE-based CaRFG2) | | | | | | | | | |
| Emissions | -21% | -21% | -21% | -34% | -25% | -12% | -13% | -4% | -32% |
| Air Quality ^a | -18% | -28% | -11% | -33% | -43% | -25% | -25% | -5% | -34% |
| 2003 Ethanol Blend at 2.0 wt% Oxygen | | | | | | | | | |
| Emissions | -21% | -21% | -21% | -35% | -27% | -6% | -15% | 37% | -100% |
| Air Quality ^a | -18% | -28% | -11% | -34% | -45% | -23% | -27% | 40% | -100% |
| 2003 Ethanol Blend at 3.5 wt% Oxygen | | | | | | | | | |
| Emissions | -26% | -21% | -21% | -33% | -26% | 15% | -15% | 59% | -100% |
| Air Quality ^a | -24% | -28% | -11% | -32% | -44% | 4% | -27% | 63% | -100% |
| 2003 Non-Oxygenate | | | | | | | | | |
| Emissions | -18% | -21% | -21% | -38% | -27% | -13% | -16% | -5% | -100% |
| Air Quality ^a | -16% | -28% | -11% | -36% | -45% | -26% | -27% | -5% | -100% |

^aAir quality changes are based on changes in population-weighted daily-average model results for gridded region.

Table 4.12. Comparison of Emission and Modeled Air Quality Changes from 2003 MTBE Baseline

| Scenario / Type of Change | CO | NO _x (NO ₂) | NO _x (HNO ₃) | Benzene | Butadiene | Acetaldehyde (Primary) | Formaldehyde (Primary) | Ethanol | MTBE |
|---|-----|---------------------------------------|--|---------|-----------|---------------------------|---------------------------|---------|-------|
| 2003 Ethanol Blend at 2.0 wt% Oxygen | | | | | | | | | |
| Emissions | 0% | 0% | 0% | -1% | -2% | 6% | -2% | 43% | -100% |
| Air Quality ^a | 0% | 0% | 0% | -3% | -2% | 4% | -3% | 48% | -100% |
| 2003 Ethanol Blend at 3.5 wt% Oxygen | | | | | | | | | |
| Emissions | -6% | 0% | 0% | 1% | -1% | 30% | -3% | 67% | -100% |
| Air Quality ^a | -7% | 0% | 0% | 1% | -2% | 39% | -3% | 72% | -100% |
| 2003 Non-Oxygenate | | | | | | | | | |
| Emissions | 4% | 0% | 0% | -7% | -2% | -1% | -4% | 0% | -100% |
| Air Quality ^a | 2% | 0% | 0% | -5% | -2% | -1% | -4% | 0% | -100% |

^aAir quality changes are based on changes in population-weighted daily-average model results for gridded region.

5. On-Going Efforts to Address Uncertainties

Our predictions of future emissions and air quality provide only an initial estimate because of significant data gaps: 1) several uncertainties in how oil refiners will reformulate gasoline in response to California's Phase 3 regulations (ARB, 1999a; 1999d), a possible waiver from the oxygenate requirement of federal RFG and market forces; 2) uncertainties in the inputs and mathematical formulation of the photochemical model; and 3) incomplete ambient measurements for some of the air contaminants. The fourth component of our analysis is to close these data gaps as part of this study and continue on-going efforts that will not be completed until after the December 31, 1999 deadline specified in the Executive Order. We report here the results of a limited emission testing program with two commercial MTBE-free CaRFG2 gasolines that provide a reality check on the emission estimates, and the progress in our long-term efforts to improve the photochemical model and collect ambient air quality data.

5.1. Emission Testing

The availability of both ethanol-blended and non-oxygenated commercial CaRFG2 gasolines presented the opportunity to provide a reality check on the organic gas emission profiles developed in Section 4.1.1. Because of the limited time available to conduct our analysis, we were neither able to test a fully representative number of vehicles nor conduct tests of diurnal or running loss evaporative emissions. We conducted emission testing at the ARB laboratory in El Monte. Full details are presented in Appendix A. We tested three fuels:

- ARB commercial MTBE-based Phase 2 regular-grade gasoline.
- Tosco ethanol-blended regular-grade gasoline (with oxygen content of 2.05 wt%).
- Chevron non-oxygenated regular-grade gasoline.

The measured fuel properties are summarized in Table 5.1.

Table 5.1. Properties for Three Commercial Fuels

| Fuel | EtOH (wt%) | MTBE (wt%) | Benzene (vol%) | Aromatics (vol%) | RVP (psi) | T50 (deg F) | T90 (deg F) | Sulfur (ppm) | Olefins (vol%) |
|----------------|-----------------------|-----------------------|---------------------------|-----------------------------|----------------------|------------------------|------------------------|-------------------------|---------------------------|
| MTBE | 0.00 | 10.67 | 0.57 | 23.9 | 6.79 | 201.0 | 311.0 | 14.00 | 3.60 |
| Ethanol | 5.88 | 0.00 | 0.42 | 28.0 | 6.88 | 203.8 | 316.4 | 1.22 | 0.21 |
| NonOxy | 0.00 | 0.00 | 0.16 | 25.0 | 6.71 | 202.1 | 303.2 | 29.20 | 3.43 |

We conducted full VOC speciation of the liquid gasoline, the headspace vapors, and exhaust tests of seven vehicles. The Tosco and Chevron gasolines are not representative of fuels expected to be sold in 2003, and we were not able to draw quantitative conclusions. Most importantly, the sulfur content is very low (~1 ppm) in the ethanol-blended gasoline; and in the non-oxygenated gasoline it is much higher (29 ppm) than the approved CaRFG3 flat limit for sulfur of 20 ppm (ARB, 1999a; 1999d). Also, the RVP and olefin content of the ethanol-blended

gasoline were lower than is expected for future ethanol-blended CaRFGs (under the approved variable-RVP provision). Gasolines with more reasonable values of sulfur, olefins, and RVP could have substantially different compositions than did the test gasolines. In addition, most of the vehicles were aged (mean model year was 1981), and several had unstable emission rates (up to a factor of five).

With these limitations in mind, the test results are consistent for several broad categories of organic gases, with the emission profiles prepared by ARB and by Professor Harley using limited data. Except for the olefins, the headspace to liquid fuel ratios for species are similar for the commercial gasolines and the predicted profiles by Professor Harley. As in the profiles, isobutene is reduced and alkylates are increased in the emissions from the MTBE-free test gasolines than from the MTBE-blended test gasoline. As in the profiles, the formaldehyde is slightly greater from the ethanol-blended test gasoline than from the non-oxygenated test gasoline, and the acetaldehyde is substantially greater. However, the ratio for acetaldehyde from the ethanol-blended test gasoline is much higher than in the profiles. Unlike the profiles, the exhausts from the MTBE-free gasolines were higher in aromatics and olefins than was the exhaust from MTBE-blended test gasoline. With consideration of the problems in the test design and the data variability, the test results do not contradict the model profiles.

5.2. Improvements in Photochemical Models

Photochemical models have uncertainties in their mathematical formulation, representations of physical and chemical process (e.g., deposition, diffusion, photochemistry), and model inputs for emissions, meteorology, and air quality. We are currently funding research to quantify model uncertainty, and to improve the model's representations of horizontal diffusivity, mixing heights, and photolysis. We are currently processing the measurements collected during the 1997 Southern California Air Quality Study (SCOS97-NARSTO) to prepare model inputs. This effort will result in improved representations of meteorology and boundary conditions (especially above the surface) for more recent ozone episodes than the 1987 case. There is much more research in these areas being conducted nationally. As model improvements become available, particularly in the area of improved chemistry for ethanol and the alkylates, we will determine their impact on our conclusions.

5.3. Ambient Air Quality Measurement Program

Our analysis of air quality impacts should be confirmed with field measurements that take place before and after the planned December 31, 2002 phase-out of MTBE. These types of studies were already conducted in California during the implementation of CaRFG2 in 1996 (Kirchstetter and Harley, 1999ab; Gertler *et al.*, 2000; Larsen, 2000). California's existing ambient air quality networks should be sufficient for all the criteria pollutants, MTBE, toxic air contaminants, and individual VOC compounds (i.e., alkylates). However, ethanol and PAN are not part of any routine air monitoring program.

In November 1999, we started a PAN and PPN monitoring program at two sites in the SoCAB. Since ethanol and acetaldehyde lead to PAN but not to PPN, the PPN-to-PAN ratio may be a useful indicator of the impact of ethanol on PAN air quality. During 1987, high PAN concentrations were observed at coastal sites (up to 19 ppb) during the winter and at Claremont (up to 30 ppb) during the summer (Grosjean, 1999b). Therefore, we are conducting year-around

measurements at a high precursor site (Burbank) and a high ozone site (Azusa). Both sites are part of the Photochemical Assessment Monitoring Stations (PAMS) program and have daily (eight 3-hour averages) speciated hydrocarbon data for three months during the summer, and 24-hour averages on a one-day-in-six schedule year-around. Burbank is an existing toxic air contaminant (TAC) monitoring site and we moved the existing sampler at Fontana to Azusa so that we will have year-around 24-hour-average formaldehyde and acetaldehyde data on a one-day-in-twelve schedule. The existing hourly ozone, NO, NO₂, and temperature measurements at Azusa and Burbank, coupled with the speciated hydrocarbon and aldehyde measurements, will allow us to conduct a thorough analysis of the effects of precursors and thermal decomposition on PAN and PPN concentrations. We will investigate the possibility of adding ethanol measurements to the TAC program in the future. Fung (1999) has proposed that data on ambient ethanol might be recovered from gas chromatograms if a gas chromatography-flame ionization detector (GC-FID) with a DB column is used to measure ambient VOCs.

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